# METHODS FOR SALT ANALYSIS

5th edition

August 2022



# Major points of the revision

- 1. The description was revised so that the sample volume can be adjusted in accordance with the conditions of the apparatus for determination of mercury.
- 2. Precautions regarding potassium hydroxide elution when using the ion chromatography are described.

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**Revision History** 

1961	JMC'S SALT ANALIZING METHODS (Salt Testing Methods )
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- 1969SALT ANALIZING METHODS (Salt Testing Methods)amended by The Japan Monopoly Corporation
- 1982 JTS METHODS FOR SALT ANALYSIS established by The Japan Tobacco & Salt Public Corporation
- 1989 METHODS FOR SALT ANALYSIS

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- 1997 METHODS FOR SALT ANALYSIS (1st edition : No English Version) established by The Salt Industry Center of Japan
- 2002 METHODS FOR SALT ANALYSIS 2nd edition established by The Salt Industry Center of Japan
- 2010 METHODS FOR SALT ANALYSIS 3rd edition established by The Salt Industry Center of Japan
- 2015 METHODS FOR SALT ANALYSIS 4th edition established by The Salt Industry Center of Japan

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# METHODS FOR SALT ANALYSIS

# 1. SCOPE OF APPLICATION

This booklet describes the chemical analysis methods required for the evaluation and inspection of salts, which include sea salt, solar salt, rock salt, lake salt, and their equivalents.

# 2. GENERAL RULES

2.1 Reagents and Apparatus

(1) The reagents used in chemical analyses of salts shall, in principle, be of analytical grade, standardized by the Japanese Industrial Standards (JIS). (The JIS specifications are similar to those of the Committee on Analytical Reagents of the American Chemical Society.)

(2) Standard solutions and standard stock solutions used in chemical analyses of salts shall be prepared from standard reagents or reagents of analytical grade.

(3) The standard stock solution shall be prepared from a reagent by taking out quickly an approximate amount of the reagent specified for the solution. The concentration of the solution shall be corrected by a factor (f), the value of which is obtained as the ratio of the amount actually taken out to the amount specified.

(4) For the standard solution, the one to provide for the preparative procedure by each examination or the one traceable to the national measurement standards can be used.

(5) Standard stock solutions can be stored, and a standard solution is prepared by diluting the corresponding standard stock solution to a definite concentration for each analysis.

(6) Acids and aqueous ammonia without their concentrations in this booklet are the commercially available concentrated acids and concentrated aqueous ammonia, respectively. Their concentrations are shown in Table 1.

Reagent	Chemical formula	Content	Molar concentration	Density
		(wt %)	(approx.) (mol/L)	(g/mL)
Hydrochloric acid	HCl	35.0 to 37.0	11.7	1.18 (15 °C)
Nitric acid	HNO <sub>3</sub>	60.0 to 62.0	13.4	1.38 (15 °C)
Sulfuric acid	$H_2SO_4$	95.0 or more	17.8 or more	1.84 (15 °C)
Acetic acid	CH <sub>3</sub> COOH	99.5 or more	17.4 or more	1.05 (20 °C)
Aqueous ammonia	NH <sub>3</sub>	28.0 to 30.0	15.4	0.90 (15 °C)
Hydrofluoric acid	HF	46.0 to 48.0	27	1.14 (20 °C)

Table 1 Chemical formulas, concentrations and densities of reagents

(7) The concentration of a liquid reagent is expressed as the volume ratio of a commercially available reagent to water required for dilution and given in the parenthesis. For example, hydrochloric acid (1+2) represents the hydrochloric acid solution prepared by diluting 1 volume of hydrochloric acid with 2 volumes of water.
(8) The concentration of a solid reagent in a solution prepared by dissolving a certain amount of the reagent

in water is given in % in the parenthesis as the amount of the reagent in the anhydrous form (in units of g) per 100 mL of the solution. For example, barium chloride solution prepared by dissolving 10 g of barium chloride dihydrate (BaCl<sub>2</sub>·2H<sub>2</sub>O) in water and dilute the resultant solution to 100 mL is represented as barium chloride solution (8.5 %).

(9) The water types used for this test shall be A1 to A4 (Table 2), as specified in JIS K 0557. When the water type is specified in an item, however, the specified type of water shall be used.

Itana	Type and quality			
Item	A1	A2	A3	A4
Electric conductivity mS/m (25°C)	0.5 or less	0.1 or less	0.1 or less	0.1 or less
Total organic carbon (TOC) mg-C/L	1 or less	0.5 or less	0.2 or less	0.05 or less
Zinc µgZn/L	0.5 or less	0.5 or less	0.1 or less	0.1 or less
Silica µgSiO <sub>2</sub> /L	-	50 or less	5.0 or less	2.5 or less
Chloride ion µgCl <sup>-</sup> /L	10 or less	2 or less	1 or less	1 or less
Sulfate ion µgSO4 <sup>2-</sup> /L	10 or less	2 or less	1 or less	1 or less

Table 2Water type and quality1)

1) Japanese Industrial Standards K 0557

(10) Filter papers shall, in principle, be No.5B type filter papers (9 or 11 cm in diameter) standardized by JIS P 3801 [filter paper (for chemical analysis)].

(11) Glassware and porcelain shall, in principle, be those standardized by JIS R 3505 and JIS R 1301 to R 1307 (for chemical analysis).

(12) Unless otherwise specified, silica gel is used for the drying agent in desiccators.

2.2 Methods for Weighing Solids and Measuring Liquids

(1) Methods for weighing solids

To weigh a solid sample or reagent, a balance (a chemical balance or an electrobalance) on which it can be weighed to the nearest 0.1 mg shall be used. In case no specification is given, an even balance on which a solid sample or reagent can be weighed to the nearest 0.1 g shall be used.

In expressing the weight (amount) of a solid, the term "approximately" means the actual weight is close to the figure specified. An even balance shall be used when weighing a solid if "approximate" is not specified. The term "accurately" or "exactly" means the solid is to be weighed to the nearest 0.1 mg on a balance. The phrase "weigh approximately 5 g exactly" means that a solid whose weight is close to 5 g is weighed to the nearest 0.1 mg on a balance.

(2) Methods for measuring liquids

Chemical volumeters shall, in principle, be those standardized by JIS R 3503 (glass chemical volumeters). Automatic burettes can also be used.

In expressing the volume of a liquid, the term "approximately" means the actual volume is close to the figure specified. A measuring cylinder shall be used when measuring the volume if "approximately" is not specified. The term "exactly" or "a definite volume" means the volume shall be measured by a whole pipette, a measuring flask, or a burette.

(3) The titration volume shall be read out to the nearest 0.01 mL.

#### 2.3 Temperature

# (1) Standard temperature

The standard temperature means 20 °C and the ordinary temperature 15 to 25 °C. The temperature difference is expressed in °C.

# (2) Analytical temperature

The analysis shall be carried out at a constant temperature.

#### (3) Water temperature

Warm water means water of 40 to 60 °C, hot water means water of 60 °C or higher, and cool water means water of 15 °C or lower.

# 2.4 Calibration of Apparatus

The chemical volumeters and the titration volume shall be calibrated in accordance with JIS R 3505 and JIS K 8006.

## 2.5 Analytical Methods

(1) The reference methods can be used within their application ranges.

(2) If the content of a major component is lower than the lower limit of the application range of the method described in Chapter 4 "Major Components", it is desirable to determine the component by the method described in Chapter 5 "Principal Trace Components".

(3) Specific attention to be drawn in carrying out chemical analyses is summarized in "Remarks". The remark number in "Remarks" is shown as a superscript in the parenthesis, <sup>()</sup>, in the text.

(4) In equations used in calculations, the symbol f denotes the factor, F titer, A, B, C and D titration volumes for sample solutions, a and b titration volumes for standard solutions, and L the limiting content.

# 2.6 Calculation, Expression and Report of Analytical Results

(1) The analytical result of a component shall be expressed as content in % or mg/kg in the sample salt as prepared (wet basis). In principle, the mg/kg expression shall be used for expressing the content less than 100 mg/kg.

(2) The data shall be rounded off by the method specified in JIS Z 8401.

(3) The analysis must be carried out in a laboratory on two sample salts prepared from the salt submitted for the analysis.

(4) The analytical result of each component shall be calculated on the basis of the corresponding equation and given as the numeral of (n + 1) figures where *n* is the number of figures specified in Table 3.

(5) When the difference in measured value between the two samples does not exceed the tolerance, the mean of the two measured values shall be calculated and reported after rounded off to a numeral specified in Table 3.

(6) The tolerance for trace components is, in principle, 10 % of the mean.

(7) When the difference in measured value between the two samples exceeds the tolerance, the analysis must be carried out again starting from the preparation of the sample salt.

(8) When the analysis is carried out based on the reference method, the name of the method must be stated expressly.

Expression	Range	Number of figures
%	0.10 % or more 2 places of decimals	
	0.010 to 0.10 %	3 places of decimals
	less than 0.010 %	2 significant figures
mg/kg	less than 100 mg/kg	2 significant figures

 Table 3
 Expression and the number of figures of results to be reported

# 2.7 Others

(1) Operations and general rules for the atomic absorption spectrometry, the absorption spectrophotometry, the emission spectrometry and the ion chromatography must be referred to those of JIS K 0121, JIS K 0115, JIS K 0116 and JIS K 0127, respectively.

(2) Items not specified in the general rules in this booklet, must be carried out in accordance with JIS general rules for chemical analysis (JIS K 0050).

# 3. PREPARATION OF SAMPLE SALTS

# 3.1 Principle

The sample salt is prepared by mixing the salt submitted for the analysis.

# 3.2 Apparatus

(1) Porcelain mortars <sup>(1)</sup>: ones with the inner diameter of about 25 cm.

(2) Polyethylene bags<sup>(2)</sup>: durable ones of about 0.07 mm thick with the dimension of approximately 20 cm wide and 25 cm long.

# 3.3 Procedure <sup>(3)</sup>

(1) In case the submitted salt is coarse grain (2 mm or larger) free <sup>(4)</sup>, put all the salt into a polyethylene bag and seal up the bag. Mix the salt well, open the bag, and take out an appropriate amount of the salt to obtain the sample salt.

(2) In the case where the submitted salt contains some coarse grains, put all of the salt into a polyethylene bag, seal up the bag, and then mix the salt well in the same way as described in (1). Take approximately 50

g of the salt out of the bag, place it in a porcelain mortar and then grind it with a pestle. Put the ground salt into a 500-mL wide-mouthed reagent bottle or polyethylene bag, shake the bottle or bag well and then discard the salt. Then, take approximately 50 g of the salt out of the bag, grind it quickly in the porcelain mortar until the grain size is approximately equal to or less than 2 mm<sup>(5)</sup>, and then put the ground salt into the 500-mL wide-mouthed reagent bottle or polyethylene bag, from which the initially ground salt was discarded. Repeat this procedure five times. Shake the bottle or bag well to mix the salt thoroughly and then take an appropriate amount of salt from the bottle or bag to be used as the sample salt.<sup>(6)</sup>

#### 3.4 Remarks

(1) In the case where the loss of water is confirmed to be small, a mill can be used.

(2) After the submitted salt is put into a polyethylene bag, pinch the mouth of the bag and inflate it by squeezing it at the position about 5 cm down from the mouth so as to make it easy to mix the salt. In the case of the bag whose mouth can be sealed tightly, caution shall be drawn so that the mouth of the bag will not open by chance when mixing the salt.

(3) The method herein described is a fundamental one for mixing the submitted salt to prepare the sample salt. Any other method, however, may be adopted if it is possible to minimize the change in water content of the submitted salt and mix it sufficiently well during the preparation of the sample salt.

(4) In case the submitted salt includes salt of coarse grains like solar salt, follow the procedure specified in item 3.3(2). Stop grinding when the grain size becomes equal to or slightly smaller than 2 mm, because salt in fine particles whose grain sizes are less than 2 mm is apt to change its water content.

(5) Mixing and grinding are to be carried out quickly, since the water content of the sample salt is apt to change with the temperature and the humidity of the working surroundings, which is a major cause of the error in analysis.

(6) In principle, the sample salt is to be prepared just before the analysis. In case it takes a certain period of time from the preparation of the sample salt to the analysis, complete at least the process of taking out an appropriate amount of the sample salt and weighing it accurately just after the preparation of the sample salt.

# 4. MAJOR COMPONENTS

Major components are defined as the components whose contents are used to calculate the amount of sodium chloride (%) in the sample salt. This chapter describes the analytical methods for those components, and each method except the one for the chloride ion is applicable if the content of the component to be measured by the method is above the lower limit of the application range of the method. In case the content is below the lower limit of the application range, the method described in Chapter 5 "Principal Trace Components" shall be used.

# 4.1 Preparation of Sample Solution

# 4.1.1 Principle

A certain amount of the sample salt is dissolved in water and the resultant solution is diluted to a definite volume to obtain the sample solution.

#### 4.1.2 Procedure (1),(2)

(1) Take out approximately 10 g of the sample salt, weigh it accurately, transfer it into a 300-mL beaker, and add 100 mL of water. Warm the solution to over 50 °C  $^{(3)}$  and dissolve the salt as much as possible by shaking the beaker well  $^{(4)}$ .

(2) Filter the solution through a filter paper <sup>(3)</sup> and wash the residue on the filter paper 6 or 7 times with 5 or 6 mL of water at each time. Then, take out a few drops of the last washing water used and make sure that it is free from the chloride ion <sup>(5)</sup>. In case the washing is insufficient, repeat it for several times more until no chloride ion is detected.

(3) Add used washing waters to the filtrate, cool the solution to room temperature, transfer it to a 500-mL measuring flask <sup>(6)</sup>, and dilute it to the mark with water to obtain the sample solution.

(4) Prepare two separate sample solutions from the same sample salt independently. For the determination of a component, take a portion out of each of the two sample solutions and analyze the two portions independently to obtain two measured values for the component.

# 4.1.3 Remarks

(1) When the sample salt contains much insoluble matter or the determination of insoluble matter and the preparation of the sample solution are carried out simultaneously, use a glass fiber filter instead of a filter paper and operate in accordance with item 4.3.

(2) Make sure in advance that the water used in this procedure is free from the chloride ion in the following way. Put approximately 100 mL of water into a 300-mL beaker, place it on a black paper, and add a few drops of silver nitrate solution (0.1 mol/L). Observe the solution carefully and make sure there is no turbidity in the solution.

(3) In case the sample salt contains only a very small amount of insoluble matter, warming and filtration are not required.

(4) Salt containing insoluble calcium or magnesium salts can be dissolved with the addition of a small amount of hydrochloric acid when the total amount of calcium or magnesium is to be measured. The analyses shall be conducted according to the items.

(5) For the test of the trace chloride ion contained in the washing water used, put approximately 5 mL of silver nitrate solution (0.1 mol/L) into a test tube and add one or two drops of nitric acid. After the tube is placed on a black paper, add the washing water to be tested drop by drop into the tube with the occasional shaking, and observe carefully whether the white turbidity of silver chloride is formed or not.

(6) A calibrated measuring flask must be used in this procedure.

# 4.2 Weight Loss on Drying (Method of drying at 140 °C)

# 4.2.1 Principle

The sample salt is dried at 140 °C for 90 minutes, and the weight loss on drying of the sample salt is obtained as the weight difference before and after drying  $^{(1)}$ .

# 4.2.2 Apparatus

(1) An electric drying oven <sup>(2)</sup>

Use the one capable of being controlled at  $140\pm2$  °C, with the capacity of 50 L or more.

(2) Weighing bottles: ones with 50 mm in diameter (JIS R 3505).

# 4.2.3 Procedure

(1) Dry a weighing bottle at 140 °C until a constant weight is reached <sup>(3)</sup>, put approximately 10 g of the sample salt just prepared into the bottle, and weigh it accurately.

(2) Place the weighing bottle in the electric drying oven <sup>(4)</sup> controlled at 140 °C, take off the cap of the bottle, and dry the bottle at 140 °C for 90 minutes.

(3) Put the cap on the bottle, allow the bottle to cool to room temperature in a desiccators <sup>(5)</sup>, and weigh it accurately.

# 4.2.4 Calculation and Expression

(1) The weight loss on drying (%) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Weight loss on drying (%) = 
$$\frac{\text{Weight loss on drying (g)}}{\text{Amount of sample salt used (g)}} \times 100$$

(2) Tolerance

Weight loss on drying (%)	Tolerance (%)
less than 0.20	0.050
0.20 to 1.00	0.100
1.00 or more	0.200

# 4.2.5 Remarks

(1) The sample salt whose total specified in item 4.8.3(2) is less than 99.50 % shall, in principle, be analyzed by the method of heating at 600 °C specified in item 7.1.

(2) It is desirable to use an electric drying oven of ventilation type that has an approximately constant temperature distribution inside.

(3) Put the weighing bottle in the oven, dry it at 140 °C for 90 minutes, allow it to cool to room temperature in a desiccator, and weigh it. Dry the bottle again at 140 °C for 30 minutes, allow it to cool to room temperature in a desiccator, and weigh it. Repeat this operation until the weight difference between two consecutive measurements becomes less than 1.0 mg. The weight of the bottle is calculated as the mean of such two measurements.

(4) The weighing bottle is to be placed on a Petri dish, a cork-plate, etc. so as not to be overheated due to the direct touch with metallic parts of the electric drying oven.

(5) Choose the number of weighing bottles placed in the desiccator at one time so that it does not exceed 60

minutes for them to cool down to room temperature.

4.3 Insoluble Matter (Method with glass fiber filters)

#### 4.3.1 Principle

The sample salt is dissolved in water. The resultant solution is filtered through a glass fiber filter with the pore size of 1  $\mu$ m, and the residue on the filter is washed with water, dried, and weighed as insoluble matter. This method is applicable when the weight of insoluble matter is 2 mg or more.

4.3.2 Apparatus

(1) An electric drying oven: the one specified in item 4.2.2(1).

(2) Glass fiber filters <sup>(1),(2)</sup>: ones with 25 to 50 mm in diameter, capable of capturing particles of 1 µm or larger.

(3) Petri dishes <sup>(1),(3)</sup>: ones with about 9 cm in diameter, made of Teflon resin.

(4) A filtration apparatus  $^{(4)}$ , one such as shown in Fig. 1.



Fig. 1 Filtration apparatus

# 4.3.3 Procedure

(1) Mount a glass fiber filter in the filtration apparatus, rinse it thoroughly by water washing with suction, take it out of the apparatus, and place it in a Petri dish. Dry the filter at 110  $^{\circ}C^{(1)}$  for 60 minutes, allow it to cool to room temperature in a desiccator, and weigh it accurately.

(2) Take out an appropriate amount of the sample salt (5 to 100 g)  $^{(5),(6)}$ , weigh it accurately, transfer it into a beaker, and add water approximately ten times as much as the amount of the sample salt taken out. Heat the solution to 50 °C or higher and stir it well to dissolve the sample salt as much as possible.

(3) Mount the glass fiber filter treated in 4.3.3(1) in the filtration apparatus and filter the solution in the beaker through the filter with suction. Rinse the beaker with about 50 mL of water and filter the rinsing water. Repeat this rinsing-and-filtering operation four or five times to transfer the insoluble matter onto the filter completely  $^{(7), (8)}$ .

(4) Take out the filter from the apparatus with a tweezers, transfer it in a Petri dish, dry it in the electric drying oven at 110  $^{\circ}C^{(1)}$  for 60 minutes, allow it to cool to room temperature in a desiccator, and weigh the filter accurately.

# 4.3.4 Calculation and Expression

(1) The content of insoluble matter (%) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Insoluble matter (%) =  $\frac{\text{Increase in weight of glass fiber filter (g)}}{\text{Amount of sample salt used (g)}} \times 100$ 

# (2) Tolerance

Insoluble matter (%)	Tolerance (%)
less than 0.05	0.010
0.05 to 0.20	0.020
0.20 or more	0.050

# 4.3.5 Remarks

(1) An organic filtration film (a membrane filter with the diameter of 25 to 50 mm and the pore size of 1  $\mu$ m) may be used instead of a glass fiber filter. In this case, the film is to be dried on a watch glass or aluminum foil at 90 °C.

(2) A glass filter crucible (type 1G4 designated by JIS R 3503) may be used as a filter.

(3) Any apparatus to which the filter does not adhere may be used.

(4) In case the filtrate is used as the sample solution for subsequent analyses (the amount of the sample salt is about 10 g), a Witt's filter apparatus equipped with an adapter shall be used instead of a suction bottle. The filtrate of the sample solution and washing waters used are collected in a beaker placed in the apparatus, transferred to a 500-mL measuring flask, diluted to the mark with water to obtain the sample solution.

(5) In case the amount of the sample salt is more than 10 g, an even balance may be used.

(6) The amount of the sample salt is chosen so that the amount of the residue on the filter is 2 mg or more. In case the sample salt contains much insoluble matter and the filter gets stuffed during the filtration, the amount of the sample salt may be 5 g or less.

(7) In case the sample salt contains much insoluble matter as colloidal suspensions, hold the sample solution for a while to sediment most of insoluble matter and start filtration first with the supernatant.

(8) Rinse out the matter adhering to the wall of the beaker and the funnel with water as much as possible, and scrape off the rest of the matter attached strongly to the wall with a policeman and the like to transfer the whole matter quantitatively onto the filter.

4.4 Chloride Ion (Titration with silver nitrate solution: Mohr method)

### 4.4.1 Principle

The sample solution is neutralized and titrated with the standard solution of silver nitrate to determine the chloride ion, using potassium chromate solution as indicator. 4.4.2 Apparatus

(1) Brown-colored burettes

(2) Platinum crucibles: ones for chemical analysis (JIS H 6201)

(3) Flasks for titration: 300-mL Erlenmeyer flasks, 300-mL conical beakers or 200-mL beakers

#### 4.4.3 Reagents

(1) Standard solution of sodium chloride  $(0.1 \text{ mol/L})^{(1)}$ 

Heat a platinum crucible at 600 °C until a constant weight is reached, and weigh it accurately. Put approximately 5.9 g of the standard reagent of sodium chloride (NaCl) (JIS K 8005) in the crucible, heat the crucible at 600 °C for 1 hour, allow it to cool in a desiccator for 30 to 60 minutes, and weigh it accurately. Dissolve the whole heated sodium chloride in water, transfer the solution into a 1-L measuring flask, and dilute it to the mark with water. This solution is stored in a tight y stoppered bottle. The solution shall not be kept for more than one month. The factor,  $f_{NaCl}$ , of the solution is calculated down to 5 places of decimals and rounded off to 4 places of decimals on the basis of the following equation:

$$f_{\text{\tiny NaCl}} = \frac{\text{Amount of sodium chloride used (g)}}{5.8443} \times \frac{\text{Purity of sodium chloride used (\%)}}{100.00}$$

(2) Potassium chromate indicator

Dissolve 5 g of potassium chromate ( $K_2CrO_4$ ) in 100 mL of water. To this solution, add silver nitrate solution drop by drop while stirring well. Filter the solution after the slightly reddish precipitate is formed. (3) Standard solution of silver nitrate (0.1 mol/L)<sup>(2)</sup>

Dissolve 17 g of silver nitrate (AgNO<sub>3</sub>) in 1 L of water and store the solution in a brown-colored bottle. The chloride ion titer,  $F_{Cl}$  (mg), per 1 mL of this solution is determined as follows:

Measure off 25 mL of the standard solution of sodium chloride (0.1 mol/L) exactly, put it into a flask for titration, add 1 mL of the potassium chromate indicator, and dilute the solution to approximately 50 mL with water. Titrate the solution with the standard solution of silver nitrate (0.1 mol/L) while stirring gently until the color of the suspension formed changes from yellow to reddish orange. The end point of titration is when the reddish orange color does not vanish any more even though the solution is stirred vigorously. The consumption of the standard solution of silver nitrate (0.1 mol/L) is denoted by "a" mL.

As the solubility of the precipitate of silver chromate appearing at the end of this titration is relatively large, the titration volume is to be corrected by a blank test. For the blank test, take out 50 mL of water, put it into a flask for titration, and add 0.5 g of calcium carbonate to obtain a suspension. Add 1 mL of the potassium chromate indicator and titrate the suspension with the standard solution of silver nitrate (0.1 mol/L) while stirring well until the color of the suspension changes from yellow to reddish orange just like the case of titration of the standard solution of sodium chloride (0.1 mol/L). The consumption of the standard solution of silver nitrate (0.1 mol/L) in this case is denoted by "b" mL <sup>(3)</sup>.  $F_{Cl}$  (mg) is calculated down to 5 places of decimals and rounded off to 4 places of decimals on the basis of the following equation:

$$F_{_{\rm CI}}$$
 (mg) = 3.5453×  $f_{_{\rm NaCl}}$  × 25.00/( $a-b$ )

# 4.4.4 Procedure

(1) Measure off exactly 10 mL of the sample solution <sup>(4)</sup> and transfer it into a flask for titration. Add 1 mL of the potassium chromate indicator and dilute the solution to approximately 50 mL with water.

(2) While stirring gently, titrate the solution with the standard solution of silver nitrate (0.1 mol/L)  $^{(5)}$  until the color of the suspension formed changes from yellow to reddish orange. The end point of titration is when the color of reddish orange does not vanish any more even though the solution is stirred vigorously. The consumption of the standard solution of silver nitrate (0.1 mol/L) is denoted by "*A*" mL.

(3) Carry out the blank test in the same way as specified in item 4.4.3(3). The consumption of the standard solution of silver nitrate (0.1 mol/L) in this case is denoted by "B" mL <sup>(3)</sup>.

#### 4.4.5 Calculation and Expression<sup>(6)</sup>

(1) The content of the chloride ion (%) is calculated on the basis of the following equation,<sup>(7)</sup> compared with the tolerance, and reported in accordance with item 2.6.

Chloride ion (%) = 
$$\frac{F_{CI} \times (A - B) \times 5}{\text{Amount of sample salt used (g)}}$$

#### (2) Tolerance

Chloride ion (%)	Tolerance (%)
25.00 or more	0.15

# 4.4.6 Remarks

(1) The standard solution of sodium chloride (0.1 mol/L) can be prepared by the following method. Weigh out approximately 5.9 g of the standard reagent of sodium chloride (NaCl) (JIS K 8005), transfer it to a porcelain crucible, heat it at 600 °C for 1 hour, and allow it to cool in a desiccator for 30 to 60 minutes. Transfer heated sodium chloride quantitatively into a weighing bottle and weigh it exactly. Dissolve it with water, transfer the solution to a 1-L measuring flask, and dilute it to the mark with water.

(2) Standardize the standard solution of silver nitrate (0.1 mol/L) before each analysis.

(3) In case the titration volume of the standard solution of silver nitrate (0.1 mol/L) in the blank test is equal to or less than that of one drop, both b and B can be regarded to be zero in the calculation.

(4) In case the sample solution is acidic or basic, titrate the sample solution after neutralization with sodium bicarbonate solution (0.1 %) or sulfuric acid (1+1000), respectively. Before the neutralization, add 1 mL of the indicator prepared by dissolving 0.2 g of *p*-nitrophenol in 100 mL of water.

(5) It is recommended in the titration that the flask for titration be placed on a white paper so that the end point is easy to observe.

(6) In the present method, amounts of bromide and iodide ions are measured as the equivalent amounts of the chloride ion. In case bromide and iodide ions are to be determined to correct the content of the chloride ion, calculate the equivalent volumes of the standard solution of silver nitrate (0.1 mol/L) and deduct them from the titration volume (consumption of the standard solution of silver nitrate (0.1 mol/L)), (A - B), on the basis of the following equations. They are to be calculated down to 3 places of decimals and rounded off to 2 places of decimals.

Titration volume  
equivalent to the amount  
of bromide ions (mL) = 
$$\frac{\text{Bromide ion obtained (%)} \times \text{Amount of sample salt used (g)}}{5 \times F_{Cl} \times 2.2538}$$
  
Titration volume  
equivalent to the amount  
of iodide ions (mL) = 
$$\frac{\text{Iodide ion obtained (%)} \times \text{Amount of sample salt used (g)}}{5 \times F_{Cl} \times 3.5795}$$

(7) The equation of item 4.4.5(1) is obtained by rearranging the following equation:

Chloride ion (%) = 
$$\frac{\frac{F_{CI} \times (A - B) \times 100}{1000}}{\frac{Amount of sample salt used (g) \times 10 (Volume of sample solution used, mL)}{500 (Volume of solution w hen sample salt is dissolved, mL)}$$

# 4.5 Calcium and Magnesium

- 4.5.1 Calcium and Magnesium (Chelatometric titration)
- 4.5.1.1 Principle

The pH of the sample solution is adjusted to 12 to 13 and calcium is determined by the titration with the standard solution of EDTA using HSNN solution as indicator. The pH of another sample solution is adjusted to 10 and the total content of calcium and magnesium is measured by the titration with the standard solution of EDTA using EBT solution as indicator. The content of magnesium is obtained by deducting the content of calcium from the total content of calcium and magnesium. This method is applicable when the contents of calcium and magnesium are both 0.02 to 1.0 %.

#### 4.5.1.2 Apparatus

(1) Burettes

(2) Flasks for titration: 200-mL Erlenmeyer flasks, 200-mL conical beakers, or 100-mL beakers.

# 4.5.1.3 Reagents

(1) Sodium hydroxide solution (4 %)

Dissolve 4 g of sodium hydroxide (NaOH) in water, dilute the solution to 100 mL, and store the solution in a polyethylene bottle.

(2) Nitrilotriethanol solution (1+10)

Mix 10 mL of 2,2',2"-nitrilotriethanol [N(CH2CH2OH)3] (triethanolamine) with 100 mL of water.

(3) Hydroxylammonium chloride solution (5 %)

Dissolve 5 g of hydroxylammonium chloride [(NH<sub>3</sub>OH)Cl] (hydroxylamine hydrochloride) in water, dilute the solution to 100 mL, transfer the solution to a brown-colored bottle, stopper the bottle tightly, and store it in a cool and dark place. This solution is stable for about one month. (4) Ammonium chloride-ammonia buffer solution (pH 10)

Dissolve 70 g of ammonium chloride (NH<sub>4</sub>Cl) in a mixed solution of 570 mL of aqueous ammonia and approximately 200 mL of water and dilute the solution to 1 L with water. (5) HSNN solution <sup>(1), (2)</sup>

Dissolve 0.5 g of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (HSNN) in 100 mL of methanol, add 0.5 g of hydroxylammonium chloride, put the solution into a brown-colored bottle, stopper the bottle tightly, and store it in a cool and dark place.

(6) Eriochrome Black T (EBT) solution <sup>(1), (3)</sup>

Dissolve 0.5 g of Eriochrome Black T (EBT) [sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2naphthol-4-sulfonate] in 100 mL of methanol, add 0.5 g of hydroxylammonium chloride, put the solution into a brown-colored bottle, stopper the bottle tightly, and store it in a cool and dark place. (7) Standard solution of EDTA (0.01 mol/L) <sup>(4)</sup>

Dry an appropriate amount of disodium ethylenediamine tetraacetate dihydrate (EDTA) at 80 °C for about 5 hours and allow it to cool in a desiccator. Weigh out approximately 3.72 g of dried EDTA exactly, dissolve it in water, transfer the solution to a 1-L measuring flask, and dilute it to the mark with water. The calcium titer,  $F_{Ca}$  (mg), and magnesium titer,  $F_{Mg}$  (mg), per 1 mL of this solution are calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equations:

$$F_{_{Ca}}(mg) = \frac{\text{Amount of EDTA used (g)}}{3.722} \times 0.4008$$
$$F_{_{Mg}}(mg) = F_{_{Ca}} \times 0.606$$
here  $0.606 = \frac{\text{Atomic weight of Mg (24.305)}}{\text{Atomic weight of Ca (40.078)}}$ 

4 5.1.4 Procedure (5)

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(1) Measure off 50 mL of the sample solution <sup>(6)</sup> exactly and transfer it into a flask for titration. Repeat this operation once more using another flask for titration.

(2) Heat one of the sample solutions at about 50 °C  $^{(7)}$ , add 10 mL of sodium hydroxide solution (4 %) to adjust pH to 12 to 13, and stir it thoroughly for about 1 minute  $^{(8)}$ .

(3) Add 1 mL of nitrilotriethanol solution  $(1+10)^{(9)}$  and 1 mL of hydroxylammonium chloride solution (5 %) and shake the solution thoroughly.

(4) Add 2 or 3 drops of the HSNN solution <sup>(2)</sup> as indicator, shake the solution thoroughly, and titrate it with the standard solution of EDTA (0.01 mol/L). The end point of titration is when the color of the solution changes from red to pure blue <sup>(10)</sup>. The consumption of the standard solution of EDTA (0.01 mol/L) is denoted by "*A*" mL.

(5) Heat the other sample solution at about 50 °C<sup>(7)</sup> and add 5 mL of the ammonium chloride-ammonia buffer

solution (pH 10) to adjust pH to 10.

(6) Add 1 mL of nitrilotriethanol solution (1+10)<sup>(9)</sup> and 1 mL of hydroxylammonium chloride solution (5 %) and shake the solution thoroughly.

(7) Add 2 or 3 drops of the Eriochrome Black T solution <sup>(3)</sup> as indicator, shake the solution thoroughly, and titrate it with the standard solution of EDTA (0.01 mol/L). The end point of titration is when the color of the solution changes from red to pure blue <sup>(10)</sup>. The consumption of the standard solution of EDTA (0.01 mol/L) is denoted by "*B*" mL.

4.5.1.5 Calculation and Expression

(1) The contents of calcium and magnesium (%) are calculated on the basis of the following equations <sup>(11)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

Calcium (%) =  $\frac{A \times F_{Ca}}{\text{Amount of sample salt used (g)}}$ Magnesium (%) =  $\frac{(B - A) \times F_{Mg}}{\text{Amount of sample salt used (g)}}$ 

(2) Tolerance

Calcium, magnesium (%)	Tolerance (%)
Less than 0.10	0.010
0.10 to 1.00	0.020

# 4.5.1.6 Remarks

(1) HSNN and EBT solutions shall not be kept for more than one month.

(2) Instead of 2 or 3 drops of HSNN solution, approximately 0.1 g of the mixed powder prepared by the following method can be used. Weigh out 0.5 g of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo) -3-naphthoic acid and 50 g of potassium sulfate. Combine the powders in an agate mortar and grind the mixture until the powders are thoroughly mixed. This indicator is to be put into a brown-colored bottle, and the bottle is stoppered tightly and stored in a desiccator so as for the indicator not to be damaged by moisture. In case the color of the solution changes from red to violet in titration instead of to pure blue, this indicator must be prepared again. The indicator is apt to be oxidized in air, and, once this occurs, it becomes difficult to recognize the color change at the end point.

(3) Instead of 2 or 3 drops of the EBT solution, approximately 0.1g of the mixed powder prepared by the following method can be used. Weigh out 0.4 g of EBT and 100 g of potassium sulfate. Combine the powders in an agate mortar and grind the mixture until the powders are thoroughly mixed. This indicator is to be put into a brown-colored bottle, and the bottle is to be stoppered tightly and stored in a desiccator.

(4) The standard solution of EDTA (0.01 mol/L) is to be anew prepared or standardized at least once a month to know the exact value of  $F_{Ca}$ . The procedure of standardization is as follows:

#### (a) Preparation of standard solution of zinc

Take out approximately 1.0 g of zinc (Zn) (JIS K 8005 or JIS H 2107), weigh it accurately, and transfer it into a 300-mL beaker. After covering the beaker with a watch glass, add 10 mL of hydrochloric acid gradually into the beaker and heat the beaker to dissolve the zinc completely. Evaporate the solution to approximately 5 mL, transfer the solution into a 1-L measuring flask, and dilute it to the mark with water. The factor,  $f_{Zn}$ , of this solution is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Zn} = \frac{\text{Amount of zinc used (g)}}{1.000} \times \frac{\text{Purity of zinc used (\%)}}{100.00}$$

(b) Standardization

Measure off exactly 10 mL of the standard solution of zinc and put it into a flask for titration. After adding 40 mL of water, heat the solution at about 50 °C. Add 5 mL of the ammonium chloride-ammonia buffer solution (pH 10) and 2 or 3 drops of EBT solution, and titrate the solution with the standard solution of EDTA (0.01 mol/L). The end point of titration is when the color of the solution changes from red to pure blue. The consumption of the standard solution of EDTA (0.01 mol/L) is denoted by "C" mL. The calcium and magnesium titers,  $F_{Ca}$  and  $F_{Mg}$ , per 1 mL of the standard solution of EDTA (0.01 mol/L) are calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equations:

$$F_{Ca} (mg) = \frac{10 \times 1 \times f_{Zn}}{C} \times 0.613$$
$$F_{Mg} (mg) = F_{Ca} \times 0.606$$
where  $0.613 = \frac{\text{Atomic weight of Ca (40.078)}}{\text{Atomic weight of Zn (65.39)}}$ 

(5) In case the phosphate ion coexists at high concentration, the end point becomes difficult to detect. In that case, it is recommended to carry out titration slowly after adding 1 mL of sodium citrate solution (0.5 mol/L) and mixing the resultant solution well in items 4.5.1.4(2) and (5). To prepare the sodium citrate solution (0.5 mol/L), dissolve 14.7 g of trisodium citrate dihydrate in water and dilute it to 100 mL with water. (6) In case one of the contents of calcium and magnesium is not within the range of 0.02 to 1.0 %, the amount of sample salt or the volume of the sample solution used for the analysis is to be increased or decreased so that both the contents fall within the range.

(7) The solution is heated to accelerate the reaction occurring in the titration because it is slow. However, the temperature of the solution must not be over 60 °C. Titration can be done at ordinary temperature but the standard solution of EDTA (0.01 mol/L) must be added slowly near the end point of titration. When the sample salt contains the phosphate ion, similar attention should be paid.

(8) In case the sample salt does not contain magnesium, titration can be carried out immediately after sodium hydroxide solution (4 %) is added.

(9) In case iron does not coexist, addition of nitrilotriethanol solution (1+10) is not required, because the purpose of adding nitrilotriethanol solution (1+10) is to prevent the interference from iron with the color change of the indicator.

(10) A photometer can be used to recognize the end point. In this case, the wavelength of the measurement

must be near 530 or 630 nm and the stable absorbance must be read out after the color changes. The end point is the point of inflection of the absorbance.

(11) The equations of item 4.5.5(1) are obtained by rearranging the following equations:

Calcium (%) =	$A \times F_{\rm Ca} \times \frac{100}{1000}$
	A mount of sample solt used (a) $50$ (Volume of sample solution used, mL)
	Amount of sample salt used (g) $\times \frac{1}{500}$ (Volume of solution when sample salt is dissolved, mL)
	(B-A)× $F_{\rm Mg}$ × $\frac{100}{1000}$
Magnesium (9	$0) = \frac{1}{2} \int (\sqrt{2} \ln \omega x + \frac{1}{2} \ln \omega x +$

 $\frac{50 \text{ (Volume of sample solution used, mL)}}{\text{Amount of sample salt used (g)} \times \frac{50 \text{ (Volume of sample solution used, mL)}}{500 \text{ (Volume of solution when sample salt is dissolved, mL)}}$ 

# 4.5.2 Calcium and Magnesium (ICP-Optical Emission Spectrometry)

# 4.5.2.1 Principle

The sample salt is dissolved in water, and the resultant solution is sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength characteristic of calcium or magnesium is detected, and the emission intensity at the characteristic wavelength is measured to determine calcium or magnesium. This method is applicable when the content of the calcium or magnesium is in the range of 0.01 to 0.10 %.

## 4.5.2.2 Apparatus

(1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer)

The apparatus shall be used with a plasma torch and a nebulizer for high salt concentration, regulated in accordance with its manual.

## 4.5.2.3 Reagents

# (1) Standard stock solution of calcium (0.4 mg/mL)

Dry approximately 2 g of calcium carbonate (CaCO<sub>3</sub>) at 110 to 150 °C for 2 hours and allow it to cool in a desiccator. Weigh out approximately 1.0 g of dried calcium carbonate exactly and transfer it to a 200mL beaker. After covering the beaker with a watch glass, dissolve calcium carbonate inside by adding 5 mL of hydrochloric acid (1+1). Heat the solution to expel carbon dioxide, cool it to room temperature, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Ca}$  is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{Ca} = \frac{\text{Amount of calcium carbonate used (g)}}{1.000}$$

# (2) Standard solution of calcium (0.1 mg/mL)

Measure off exactly 25 mL of the standard stock solution of calcium (0.4 mg/mL) (1), transfer it to a 100-mL measuring flask, add 1 mL of hydrochloric acid (1+1), and dilute the solution to the mark with water.

(3) Standard stock solution of magnesium (1 mg/mL)

Weigh out approximately 1.0 g of magnesium metal exactly and transfer it to a 200-mL beaker. After covering the beaker with a watch glass, dissolve magnesium inside with 15 mL of hydrochloric acid, transfer the solution to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Mg}$  is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{Mg} = \frac{\text{Amount of magnesium carbonate used (g)}}{1.000}$$

(4) Standard solution of magnesium (0.1 mg/mL)

Measure off exactly 10 mL of the standard stock solution of magnesium (1 mg/mL) (3), transfer it to a 100-mL measuring flask, add 5 mL of hydrochloric acid (1+1), and dilute the solution to the mark with water.

(5) Sodium chloride: the standard reagent of sodium chloride (NaCl) (JIS K 8005)

(6) Argon gas

# 4.5.2.4 Procedure

(1) Prepare the sample solution in accordance with item 4.1  $^{(1),(2),(3)}$ .

(2) Regulate the ICP spectrometer, spray the sample solution into the plasma torch, and measure the emission intensity <sup>(4)</sup> at the wavelength of 393.367 nm for calcium or 279.553 nm for magnesium <sup>(5)</sup>. Obtain the amount of calcium or magnesium (mg) from the calibration curve prepared separately.

# 4.5.2.5 Preparation of Calibration Curve

Measure off stepwise definite volumes (0 to 20 mL) of the standard solutions of calcium and magnesium<sup>(6)</sup>, transfer the solutions to respective 100-mL measuring flasks, and add 2 g of sodium chloride to each solution.
 After dissolving the sodium chloride completely, dilute each solution to the mark with water. Carry out the procedure specified in item 4.5.2.4(2) to determine the relationship between the amount of calcium or magnesium (mg) and the emission intensity to obtain the calibration curve.

#### 4.5.2.6 Calculation and Expression

(1) The content of calcium or magnesium (%) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Calcium or Magnesium (mg/kg) =  $\frac{\text{Amount of calcium or magnesium obtained (mg)} \times 0.5 \times f}{\text{Amount of sample used (g)}}$ 

where f is the factor of the standard stock solution of each component.

## (2) Tolerance

Calcium, magnesium (%)	Tolerance (%)
0.01 to 0.10	0.010

# 4.5.2.7 Remarks

In case trace amounts of calcium and magnesium (less than 0.01 %) are to be measured, prepare the sample solution and analyze it in accordance with item 5.1.2. In case the contents of calcium and magnesium larger than 0.10 %, dilute the sample solution before measurement and adjust the concentration of sodium chloride in the standard solutions for the calibration curve to the same as that of the diluted sample solution.
 In case the sample solution contains insoluble matter, filter it with a dried filter paper (No. 5C). In this case, discard the first 5 mL of the filtrate, and use the rest for the analysis.

(3) In case the nebulizer is plugged while spraying the sample solution, filter the sample solution before use.

(4) The background correction must always be done to obtain the accurate emission intensity.

(5) When the high order spectral lines can be used in the apparatus, they may be used for the analysis. In the selection of the wavelength for an element, make sure that there is no interference from closely located spectral lines of other elements.

(6) Adjust the concentrations of the standard solutions for the calibration curve in accordance with the sensitivity of the apparatus for the element to be determined and its content in the sample solution.

(7) The equation of item 4.5.2.6(1) is obtained by rearranging the following equation:

		Content (mg) $_{\times 100 \times f}$
Calcium or Magnesium (%) =		1000
	Amount of sample used $(\alpha)$	100 (Volume of sample solution used, mL)
	Amount of sample used (g)	500 (Volume of sample salt when sample salt is dissolved, mL)

4.6 Sulfate Ion

4.6.1 Sulfate ion (Barium chromate absorptiometry)

# 4.6.1.1 Principle

A suspension of barium chromate is added to the sample solution to precipitate barium sulfate, and the amount of the chromate ion, which is liberated into the solution phase through the ion exchange with the sulfate ion, is photometrically measured to determine the sulfate ion indirectly. This method is applicable when the content of the sulfate ion is 0.01 to 0.40 %.

# 4.6.1.2 Apparatus

(1) A photoelectric spectrophotometer or a photoelectric photometer

(2) Flat-bottom test tubes with ground-in stoppers <sup>(1)</sup>: those of about 23 mm in inner diameter, 50 mL in volume and with graduations.

# 4.6.1.3 Reagents

(1) Barium chromate suspension<sup>(2)</sup>

Grind a certain amount of barium chromate (BaCrO<sub>4</sub>) in an agate mortar, add 2.5 g of ground barium

(24)

chromate to the mixed solution of 100 mL of acetic acid (1 + 35) and 100 mL of hydrochloric acid (1 + 50) to obtain the barium chromate suspension.

(2) Aqueous ammonia containing calcium

Dissolve 1.85 g of calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O) to 500 mL of aqueous ammonia (1+4) and store the solution in a polyethylene bottle.

(3) Ethanol

(4) Standard stock solution of sulfate ion (1 mg/mL)

Dry approximately 2 g of potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) at 110 °C for about 1 hour and allow it to cool in a desiccator. Weigh out approximately 1.8 g of dried potassium sulfate exactly, dissolve it in water, transfer the solution to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{SO4}$  is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm SO4} = \frac{\text{Amount of potassium sulfate used (g)}}{1.814}$$

(5) Standard solution of sulfate ion (0.1 mg/mL)

Measure off exactly 50 mL of the standard stock solution of sulfate ion (1 mg/mL), transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

(6) Sodium chloride solution (10 %)

Dissolve 50 g of sodium chloride (NaCl) in water and dilute the solution to 500 mL with water.

# 4.6.1.4 Procedure

(1) Measure off 25 mL of the sample solution <sup>(3)</sup> exactly and transfer it to a 50-mL flat-bottom test tube with a ground-in stopper. After the barium chromate suspension is homogenized by thoroughly shaking, measure off 3 mL of the suspension with a measuring pipette quickly and add it to the sample solution in the tube. Shake the tube thoroughly for 1 minute and allow it to stand for 2 minutes. Repeat the shaking-allowing to stand operation once more.

(2) Add gently 1 mL of the supernatant of aqueous ammonia containing calcium with a dropping pipette <sup>(4)</sup>, add 10 mL of ethanol, and dilute the solution to the mark with water. Shake the tube for 1 minute, and allow it to stand for 10 minutes.

(3) Filter the solution through a dried filter paper (No. 5C)  $^{(5)}$ , discard the first 5 mL of the filtrate, and receive the subsequent filtrate in a 50-mL beaker. Transfer an aliquot of the filtrate to an absorption cell, measure its absorbance at the wavelength of 370 or 400 nm with water as reference, and obtain the content of the sulfate ion (mg) from the calibration curve prepared separately.

# 4.6.1.5 Preparation of Calibration Curve

(1) Measure off exactly 0, 2, 4, 6, 8 and 10 mL of the standard solution of sulfate ion (0.1 mg/mL) (correspondingly containing 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mg of the sulfate ion) or 0, 5, 10, 15 and 20 mL of

the solution (correspondingly containing 0, 0.5, 1.0, 1.5 and 2.0 mg of the sulfate ion), and transfer them to 50-mL flat-bottom test tubes with ground-in stoppers separately.

(2) Add 5 mL of sodium chloride solution (10%) to each solution and dilute the solution to 25 mL with water. Measure the absorbance of each solution following the procedure specified in items 4.6.1.4(1) to (3) Note that the absorbance of solutions containing 1.0 mg or less of the sulfate ion should be measured at 370 nm and that of solutions containing more than 1.0 mg of the sulfate ion should be measured at 400 nm. Determine the relationship between the absorbance and the amount of the sulfate ion (mg) to obtain the calibration curve. Prepare the calibration curve every time when the sample solution is analyzed.

# 4.6.1.6 Calculation and Expression

(1) The content of the sulfate ion (%) is calculated on the basis of the following equation <sup>(6)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

Sulfate ion (%) =  $\frac{\text{Amount of sulfate ion obtained (mg)} \times f_{SO4} \times 2}{\text{Amount of sample salt used (g)}}$ 

(2) Tolerance

Sulfate ion (%)	Tolerance (%)
less than 0.40	0.040

## 4.6.1.7 Remarks

(1) 50-mL measuring flasks may be used instead of flat-bottom test tubes with ground-in stoppers.

(2) Use of impure barium chromate leads to a large value in the blank test. When the purity of barium chromate is questionable, purify it before use as follows:

Dissolve 13 g of barium chromate (BaCrO<sub>4</sub>) in 100 mL of hydrochloric acid (1+5) while heating and dilute the solution to approximately 700 mL with water. Heat the solution at 70 to 80 °C and add aqueous ammonia (1+7) drop by drop to reprecipitate barium chromate. While adding aqueous ammonia (1+7), take out occasionally a portion of the solution and add to it bromothymol blue solution prepared by dissolving 0.1 g of bromothymol blue in 50 mL of ethanol and diluting the solution to 100 mL with water. Keep adding aqueous ammonia (1+7) until the color of a portion of the solution taken out changes to blue when bromothymol blue solution is added. Wash the precipitate of barium chromate a few times with approximately 500 mL of warm water at each time by decantation. After discarding the supernatant, filter the solution containing the precipitate of barium chromate through a glass filter crucible (1G4) with suction and wash the precipitate on the filter with a small amount of water a few times. Dry the precipitate at 110 °C for about 1 hour, grind it to fine powder in an agate mortar, put the powder in a wide-mouthed reagent bottle, and store the bottle in a desiccator.

(3) When the content of the sulfate ion is 0.4 % or more, decrease the volume of the sample solution measured off. In this case, decrease also the volume of sodium chloride solution (10 %) added in the preparation of

the calibration curve in the same proportion as the decrease in volume of the sample solution.

(4) When the suspension of barium chromate is added to the sample solution to precipitate barium sulfate, the pH of the solution should be 2.0 to 3.5. After the addition of the aqueous ammonia containing calcium, the pH of the solution should be 9.0 to 10.0. In case pH is out of these ranges, prepare the reagents again or neutralize the sample solution.

(5) In case the filtrate is turbid, do over again from the beginning of the procedure. Filtration may be substituted by centrifugal separation. The centrifugal separator to be used in that case should be equipped with a timer and can rotate at 3000 rpm or higher. The procedure is as follows: put the suspension into a 10-mL centrifuge tube, centrifuge it at 2500 to 3000 rpm for 10 minutes, and submit the supernatant to the analysis.

(6) The equation of item 4.6.1.6(1) is obtained by rearranging the following equation:

	Amount of su	ilfate ion obtained (mg) $\times 100 \times f$
Sulfate ion (%) =		$\frac{1000}{1000} \times 100 \times J_{so4}$
	A mount of sample salt used $(a)$	25 (Volume of sample solution used, mL)
	Amount of sample sait used (g) ×	500 (Volume of solution when sample salt is dissolved, mL)

#### 4.6.2 Sulfate Ion (Ion chromatography)

# 4.6.2.1 Principle

The sample salt is dissolved in water and the sulfate ion is determined by ion chromatography. This method is applicable when the content of the sulfate ion is 0.01 to 0.40 %.

# 4.6.2.2 Apparatus

#### (1) An ion chromatograph

The ion chromatograph should be equipped with (a) to (d) below and capable of detecting the sulfate ion. It is composed of an eluent reservoir, a pump, a sample injector, a separation column, a suppressor, a regenerant reservoir, a detector, and a recorder, as shown in Fig 2.



Fig. 2 Ion chromatograph

### (a) A separation column

Use the column capable of separating the sulfate ion from other anionic components.

# (b) A suppressor

Use an ion exchange membrane or ion exchange resin type suppressor, the function of which is to exchange cations in the eluent with hydrogen ions in the regenerant.

- (c) A detector: a conductivity detector.
- (d) A sample injector

Use the one with an injection loop of 50 or 100  $\mu$ L.

#### 4.6.2.3 Reagents

# (1) Water

Distilled water or water equivalent to or purer than it shall be used.

# (2) Eluent<sup>(1)</sup>

Sodium carbonate solution or mixed solution of sodium carbonate and sodium hydrogencarbonate with the concentration suitable for the apparatus and the separation column shall be used. It shall be degassed before use <sup>(2)</sup>.

# (3) Regenerant

Dilute sulfuric acid solution of the concentration suitable for the eluent and the suppressor shall be used. (4) Standard solution of sulfate ion  $(4 \mu g/mL)$ 

Measure off exactly 10 mL of the standard solution of sulfate ion (0.1 mg/mL) prepared in accordance with item 4.6.1.3(5), transfer it to a 250-mL measuring flask, and dilute it to the mark with water.

# 4.6.2.4 Procedure

(1) Measure off exactly 10 mL of the sample solution, transfer it to a 500-mL measuring flask, dilute it to the mark with water to obtain the sample solution for the sulfate ion (concentration of sample salt: 0.04 %) <sup>(3),(4)</sup>. (2) Regulate the apparatus in accordance with its manual, inject the sample solution for the sulfate ion and obtain the chromatogram <sup>(5),(6)</sup>. Read out the height or the area of the peak corresponding to the sulfate ion. (3) Obtain the amount of the sulfate ion ( $\mu$ g) from the calibration curve prepared separately.

# 4.6.2.5 Preparation of Calibration Curve

Measure off stepwise definite volumes of the standard solution of sulfate ion (4  $\mu$ g/mL) exactly within the range of 1 to 50 mL <sup>(7),(8)</sup>, transfer each to a 100-mL measuring flask, and dilute it to the mark with water. Carry out item 4.6.2.4(2) on each solution and determine the relationship between the amount of the sulfate ion ( $\mu$ g) and the peak height or the peak area <sup>(6)</sup> to obtain the calibration curve.

# 4.6.2.6 Calculation and Expression

(1) The content of the sulfate ion (%) is calculated on the basis of the following equation <sup>(9)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

Sulfate ion $(\%)$ –	Amount of sulfate ion obtained (µg)	$\sim 0.025 \times f$
	Amount of sample salt used (g)	$(0.023 \times J_{SO4})$

(2) Tolerance

Sulfate ion (%)	Tolerance (%)
less than 0.10	0.010
0.10 to 0.40	0.020

4.6.2.7 Remarks

(1) When a potassium hydroxide solution is used as the eluent, be aware that magnesium in the sample may precipitate as a hydroxide, which may accelerate the deterioration of the column.

(2) Degassing shall be done by the suction or ultrasonication method or the combination of the two, or with a degasifier.

(3) In case the amount of the sulfate ion is trace, the degree of dilution may be reduced. It should be checked, however, that the peak of the sulfate ion is well separated from those of other anionic components.

(4) In case the sample solution contains insoluble matter, it should be used after filtration with a membrane filter with the pore size of 0.45  $\mu$ m or less or a glass fiber filter of item 4.3.2(2). This is because insoluble matter accelerates the deterioration of the column. Note that the membrane filter shall be rinsed with water before use.

(5) After obtaining a chromatogram, check whether a fraction of the sample solution for the sulfate ion just injected remains in the apparatus or not by injecting distilled water. This procedure is not necessarily to be done at each injection but should be done in an adequate interval.

(6) A data processor for chromatography may be used for this purpose.

(7) Adjust the concentration and the volume of the standard solution of sulfate ion (4  $\mu$ g/mL) used in the preparation of the calibration curve in accordance with the estimated concentration of the sulfate ion in the sample solution for the sulfate ion and the sensitivity of the apparatus.

(8) In case two or more components are determined simultaneously, mixed standard solutions may be used.

(9) The equation in item 4.6.2.6(1) is obtained by rearranging the following equation:

Sulfate ion (%)=	Amount of sulfate ion obtained ( $\mu g$ ) $1 \times f \times 100$	
	$\frac{1000 \times 1000}{100} \times \frac{100}{100} \times \frac{100}{100} \times \frac{100}{100}$	
	Amount of sample salt used (g) $\times 10$ (Volume of sample solution used, mL)	1
	500 (Volume of solution w hen sample salt is dissolved, mL)	500

# 4.7 Potassium (Flame photometry)

#### 4.7.1 Principle

The sample solution is sprayed into the flame and the emission intensity of the bright line of potassium at the wavelength of 766.5 or 769.8 nm is measured to determine potassium. This method

is applicable when the content of potassium is 0.01 to 0.30 %.

#### 4.7.2 Apparatus

(1) A flame spectrophotometer, a flame photometer or an atomic absorption spectrometer

The apparatus is regulated according to its manual and the wavelength is adjusted to 766.5 or 769.8 nm. If so required, use the interference filter for the determination of potassium. The fuel gas is propane gas, town gas or acetylene gas, depending on the apparatus used.

# 4.7.3 Reagents

# (1) Standard stock solution of potassium (1 mg/mL)

Dry approximately 3 g of potassium chloride (KCl) at 500 to 600 °C for 40 to 50 minutes and allow it to cool in a desiccator. Weigh out approximately 1.91 g of dried potassium chloride exactly, and dissolve it in water. Transfer the solution into a 1-L measuring flask, dilute it to the mark with water, and store the solution in a polyethylene bottle. The factor of this solution,  $f_K$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\kappa} = \frac{\text{Amount of potassium chloride used (g)}}{1.907}$$

(2) Standard solution of potassium (0.1 mg/mL)

Measure off exactly 50 mL of the standard stock solution of potassium (1 mg/mL), transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

(3) Standard reagent of sodium chloride (JIS K 8005)

# 4.7.4 Procedure

(1) Measure off exactly 25 mL of the sample solution <sup>(1)</sup>, transfer it to a 100-mL measuring flask, and dilute it to the mark with water to obtain the sample solution for potassium.

(2) Regulate the apparatus <sup>(2)</sup>, spray the sample solution for potassium to the flame <sup>(3)</sup>, read out the indicated value on the scale at the wavelength of 766.5 or 769.8 nm (or the indicated value on the scale when the interference filter is used), and obtain the amount of potassium (mg) from the calibration curve prepared separately.

# 4.7.5 Preparation of Calibration Curve<sup>(1)</sup>

(1) Prepare the No. 1 to 7 standard solutions for the calibration curve specified in Table 4 as follows: Weigh out 0.5 g of sodium chloride, dissolve it in water and transfer the solution to a 100-mL measuring flask. Measure off the definite volume of the standard solution of potassium (0.1 mg/mL) specified in Table 4, add it to the measuring flask containing sodium chloride solution, and dilute the solution to the mark with water.

Solution	Volume of standard	Amount of	Amount of
number	solution of potassium	sodium chloride	potassium (mg)
	(0.1 mg/mL) added (mL)	added (g)	
1	0	0.5	0
2	1.0	0.5	0.1
3	2.0	0.5	0.2
4	4.0	0.5	0.4
5	6.0	0.5	0.6
6	10.0	0.5	1.0
7	15.0	0.5	1.5

Table 4Standard solutions for calibration curve

(2) Adjust the indicated value on the scale of the apparatus to zero by using the No.1 standard solution for the calibration curve in accordance with item 4.7.4(2).

(3) Then, spray the No.2 to No.7 standard solutions for the calibration curve successively to read out the indicated values. Determine the relationship between the amount of potassium (mg) and the indicated value to obtain the calibration curve <sup>(4)</sup>. Prepare the calibration curve every time when the sample solution for potassium is analyzed.

# 4.7.6 Calculation and Expression

(1) The content of potassium (%) is calculated on the basis of the following equation <sup>(5)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

Potassium (%) = 
$$\frac{\text{Amount of potassium obtained (mg)} \times f_{\text{K}} \times 2}{\text{Amount of sample salt used (g)}}$$

(2) Tolerance

Potassium (%)	Tolerance (%)
less than 0.10	0.010
0.10 to 0.30	0.020

# 4.7.7 Remarks

When the content of potassium in the sample salt is large (0.3 % or more), decrease the volume of the sample solution measured off. In this case, decrease also the amount of sodium chloride added in the preparation of the calibration curve in the same proportion as the decrease in volume of the sample solution.
 When potassium is determined flame photometrically with an atomic absorption spectrometer using the acetylene-air mixed gas, it is recommended that the burner head be positioned perpendicularly to the optical axis in order to reduce the sensitivity and accordingly reduce the non-linearity of the calibration curve obtained.

(3) When the indicated value fluctuates owing to the changes in flow rate of the sample solution for potassium, inflow of the fuel, and/or the voltage, analyze the sample solution for potassium and the standard solution for the calibration curve, whose concentration is closest to that of the sample solution for potassium, alternately and repeatedly as quickly as possible to minimize the influence of the fluctuation.

(4) When the apparatus with an analogue meter to show the emission intensity is used, the calibration curve may be obtained by adjusting 0 and 100 % of the meter.

(5) The equation in item 4.7.6(1) is obtained by rearranging the following equation:

	Amount of potassium obtained (mg) $\times 100 \times f$
Potassium (%) =	1000 × 100 × J <sub>K</sub>
	A mount of sample salt used $(a)$ × 25 (Volume of sample solution used, mL)
	Amount of sample sait used (g) $\times \frac{500}{500}$ (Volume of solution when sample salt is dissolved, mL)

4.8 Sodium Chloride (Calculation of combined components)

4.8.1 Principle

Sodium chloride (NaCl) and sodium (Na) are determined by calculations using the analyzed (reported) contents of other components (%).

# 4.8.2 Calculation of Content of NaCl<sup>(1),(2)</sup>

(1) First, the value of  $\alpha$  is calculated on the basis of the following equation:

 $\alpha = Ca(\%) \times 2.92 + Mg(\%) \times 4.81 - SO_4(\%) \times 1.22$ 

NaCl is determined by one of the following equations depending on the sign of the value of  $\alpha$ .

(2) When the value of  $\alpha$  is positive,

 $NaCl(\%) = Cl(\%) \times 1.6485 - K(\%) \times 1.49 - \alpha$ 

(3) When the value of  $\alpha$  is zero or negative,

 $NaCl(\%) = Cl(\%) \times 1.6485 - K(\%) \times 1.49$ 

(4) In each multiplication in the equations in items 4.8.2(1) to (3), the product is calculated down to 3 places of decimals, and  $\alpha$  and the content of NaCl (%) are rounded off to 2 places of decimals.

# 4.8.3 Total

(1) The content of sodium (%) is calculated down to 3 places of decimals and rounded off to 2 places of decimals from the content of NaCl (%) obtained in item 4.8.2 on the basis of the following equation  $^{(3)(4)}$ :

$$Na(\%) = NaCl(\%) \times 0.3934$$

If  $\alpha$  is negative, however, the content of Na (%) is obtained as follows:

 $Na(\%) = [NaCl(\%) + |\alpha|] \times 0.3934$ 

(2) The total is obtained by the following equation:

Total (%) = Weight loss on drying (%) + Insoluble matter (%) +  $Cl(\%) + Ca(\%) + Mg(\%) + SO_4(\%) + K(\%) + Na(\%)$ 

(3) The total is often within the range between 99.50% and 100.20%. Consequently, this range can be used as a measure of the correctness of each procedure.

# 4.8.4 Remarks

(1) The coefficient of the content of each component (%) in the equations in item 4.8.2 is the equivalent of the component to NaCl, namely,

Coefficient of Cl : NaCl  $(58.443) \div$  Cl (35.4453) = 1.6485Coefficient of Ca : 2NaCl  $(58.443 \times 2) \div$  Ca (40.078) = 2.92Coefficient of Mg : 2NaCl  $(58.443 \times 2) \div$  Mg (24.305) = 4.81Coefficient of SO<sub>4</sub> : 2NaCl  $(58.443 \times 2) \div$  SO<sub>4</sub> (96.062) = 1.22Coefficient of K : NaCl  $(58.443) \div$  K (39.098) = 1.49

(2) When the content of NaCl in the sample salt is 99 % or more, it may be determined by deducting the analytical values of impurities (%) from 100 (%). In this case, all the analytical results are first expressed in %, and in each multiplication, the product is calculated down to 4 places of decimals and rounded off to 3 places of decimals. Calculation shall be carried out as follows:

(a) Calculation of the content of the Cl combined with Ca and Mg, or that of sodium combined with the SO<sub>4</sub>.

- (i) The value of  $\alpha$  is first calculated on the basis of the equation in item 4.8.2(1). Calculation in (ii),
  - (iii) or (iv) below shall be done depending on the sign of the value of  $\alpha$ .
- (ii) When the value of  $\alpha$  is positive, calculate the content of the Cl (%) combined with Ca and Mg as follows:

 $Cl(Ca, Mg)(\%) = \alpha \times Cl(35.453) / NaCl(58.443) = \alpha \times 0.6066$ 

- (iii) When the value of  $\alpha$  is zero, the content of the chloride ion combined with Ca and Mg is also zero.
- (iv) When the value of  $\alpha$  is negative, calculate the content of Na combined with the SO<sub>4</sub> as follows:

 $Na(SO_4)(\%) = |\alpha| \times Na (22.990)/NaCl (58.443) = |\alpha| \times 0.3934$ 

(b) Calculation of the content of the Cl combined with potassium

Cl(K) (%) = K (%) × Cl (35. 453)/K (39. 098) = K (%) × 0.907

(c) Calculation of the content of NaCl

The content of NaCl (%) is obtained by deducting the analytical values (%) and the contents of the components (%) obtained in items 4.8.4(2) (a) and (b) from 100.000 (%). It is rounded off to 2 places of decimals and reported.

 $NaCl(\%) = 100.000 (\%) - \{Weight loss on drying (\%) + Insoluble matter (\%) + SO_4(\%) + Ca(\%) + Mg(\%) + K(\%) + [Cl(Ca, Mg) or Na(SO_4)](\%) + Cl(K)(\%) \}$ 

(3) In the case where the number of places of the analytical values lacks reliability, the value with the highest least significant digit among the significant figures can be calculated down to one digit smaller than the least significant digit, and the resultant least significant digit can be rounded off.

(4) The coefficient in the equation of item 4.8.3(1) is the equivalent of NaCl to Na, namely,

Na (22. 990)/NaCl (58.443) = 0.3934

# 5. PRINCIPAL TRACE COMPONENTS

This chapter describes the analytical methods for the components whose contents are used to calculate the content of sodium chloride (%) in the sample salt and are below the lower limits of the application ranges specified in Chapter 4.

# 5.1 Calcium and Magnesium

5.1.1 Calcium and Magnesium (Atomic Absorption Spectrometry)

# 5.1.1.1 Principle

The sample solution is sprayed into the flame of acetylene-air and the atomic absorption is measured at the wavelengths of 422.7 and 285.2 nm to determine calcium and magnesium, respectively. This method is applicable when the content of calcium is in the range of 5 to 60 mg/kg and that of magnesium is in the range of 2 to 30 mg/kg.

# 5.1.1.2 Apparatus

(1) An atomic absorption spectrometer

Use the spectrometer regulated in accordance with its manual. Acetylene gas is used as fuel gas.

(2) Calcium and magnesium hollow cathode lamps

# 5.1.1.3 Reagents

(1) Standard solution of calcium (0.04 mg/mL)

Measure off exactly 10 mL of the standard stock solution of calcium (0.4 mg/mL) specified in item 4.5.2.3(1), transfer it to a 100-mL measuring flask, add 1 mL of hydrochloric acid (1+1), and dilute the solution to the mark with water.

(2) Standard solution of magnesium (0.02 mg/mL)

Measure off exactly 10 mL of the standard stock solution of magnesium (1 mg/mL) specified in item 4.5.2.3(3), transfer it to a 500-mL measuring flask, add 5 mL of hydrochloric acid (1+1), and dilute the solution to the mark with water.

(3) Standard solution for addition

Prepare two 100-mL measuring flasks and name them No.1 and No.2. Measure off exactly definite volumes of the standard solutions of calcium (0.04 mg/mL) and magnesium (0.02 mg/mL) specified in Table 5, and dilute them to the mark with water to obtain the No. 1 and No. 2 standard solutions for addition.

Standard	Calcium		Magnesium	
solution for	Volume of standard	Conc.	Volume of standard	Conc.
addition	solution used (mL)	(µg/mL)	solution used (mL)	(µg/mL)
No.1	5	2.0	5	1.0
No.2	10	4.0	10	2.0

Table 5 Volume of standard solution taken for preparing standard solution for addition

# 5.1.1.4 Procedure

(1) Measure off exactly 25 mL of the sample solution prepared in accordance with item 4.1, transfer it to a 50-mL measuring flask <sup>(1)</sup>, dilute it to the mark with water to obtain the sample solution for calcium and magnesium. Measure off exactly 25 mL of the sample solution, transfer it to another 50-mL measuring flask <sup>(1)</sup>, add exactly 5 mL of the No. 1 standard solution for addition, dilute the solution to the mark with water, and term the solution "No.1 sample solution for standard addition". Measure off exactly 25 mL of the sample solution, transfer it to a third 50-mL measuring flask <sup>(1)</sup>, add exactly 5 mL of the No.2 standard solution for addition, dilute the solution to the mark with water, and term the solution as "No.2 sample solution for standard addition".

(2) After regulating the atomic absorption spectrometer, adjust the wavelength to 422.7 nm for calcium. Spray the sample solution for calcium and magnesium into the flame of acetylene-air and record the indicated value (absorbance) of the apparatus. Spray the No. 1 and No. 2 sample solutions for standard addition successively and record the indicated values.

(3) For the determination of magnesium, adjust the wavelength to 285.2 nm and analyze the solutions in the similar manner as item 5.1.1.4(2).

(4) Graduate the amount of calcium or magnesium added (Ca: 0, 10 and 20  $\mu$ g; Mg: 0, 5 and 10  $\mu$ g) as abscissa and the indicated value (absorbance) as ordinate on a graph paper, plot the values, connect the points with a straight line, and read out the point for the amount of calcium or magnesium (in units of µg) where the extrapolated line intersects the abscissa<sup>(2)</sup>.

5.1.1.5 Calculation and Expression

(1) The contents of calcium and magnesium (mg/kg) are calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Calcium or Magnesium (%) =  $\frac{\text{Amount of calcium and magnesium obtained }(\mu g) \times f}{\text{Amount of sample salt used }(g)}$ 

where *f* is the factor of the standard stock solution of calcium or magnesium.

# 5.1.1.6 Remarks

(1) In case the content of calcium or magnesium is out of the application range, increase or decrease the volume of the sample solution measured off.

(2) In case the linearity of the three points is not good, prepare again the sample solutions for standard addition from the beginning.

(3) The equation of item 5.1.1.5 is obtained by rearranging the following equation:

Content (µg) 1000

25 (Volume of sample solution used, mL)

Amount of sample salt used(g)  $\times \frac{25 (1.01411.0141)}{500}$  (Volume of sample salt when sample salt is dissolved, mL)
## 5.1.2 Calcium and Magnesium (ICP-Optical Emission Spectrometry)

## 5.1.2.1 Principle

The sample salt is dissolved in water, and the resultant solution is sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength characteristic of calcium or magnesium is detected and the emission intensity at the characteristic wavelength is measured to determine calcium or magnesium. This method is applicable when the content of the calcium and magnesium is in the range of 1 to 100 mg/kg and 0.1 to 100 mg/kg, respectively.

## 5.1.2.2 Apparatus

(1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer): the one specified in item 4.5.2.2(1).

## 5.1.2.3 Reagents

# (1) Standard solution of calcium (5 $\mu$ g/mL)

Measure off exactly 25 mL of the standard stock solution of calcium (0.04 mg/mL) specified in item 5.1.1.3(1), transfer it to a 200-mL measuring flask, add 2 mL of hydrochloric acid (1+1), and dilute the solution to the mark with water.

(2) Standard solution of magnesium (0.5  $\mu$ g/mL)

Measure off exactly 5 mL of the standard stock solution of magnesium (0.02 mg/mL) specified in item 5.1.1.3(2), transfer it to a 200-mL measuring flask, add 2 mL of hydrochloric acid (1+1), and dilute the solution to the mark with water.

(3) Sodium chloride: the standard reagent of sodium chloride (NaCl) (JIS K 8005)

(4) Argon gas

## 5.1.2.4 Procedure<sup>(1)</sup>

(1) Measure off exactly 5 g of the sample salt, transfer it to a 100-mL measuring flask, add 1 mL of hydrochloric acid(1+1) with an appropriate amount of water to dissolve the sample salt, and dilute it to the mark with water  $^{(2)}$ .

(2) Regulate the ICP spectrometer, spray the sample solution in the plasma torch <sup>(3)</sup>, and measure the emission intensity at the wavelength of 393.367 nm for calcium and 279.553 nm for magnesium <sup>(4), (5)</sup>. Obtain the amount of calcium or magnesium ( $\mu$ g) from each calibration curve prepared separately.

#### 5.1.2.5 Preparation of Calibration Curve<sup>(1), (6)</sup>

(1) Measure off stepwise definite volumes of the standard solution of calcium (5  $\mu$ g/mL) and magnesium (0.5  $\mu$ g/mL) exactly within the range of 1.0 to 10 mL, transfer each to a 100-mL measuring flask, add 1 mL of hydrochloric acid (1+1), and add 5 g of sodium chloride to each solution.

(2) After dissolving the sodium chloride completely, dilute each solution to the mark with water. Carry out the procedure specified in item (2) to measure the emission intensity for calcium and magnesium.

(3) Prepare another sodium chloride solution without the addition of the standard solution in the same manner

as described in (1), and measure the emission intensity of this solution. Determine the relationship between the corrected emission intensity obtained as the difference between those measured for the solutions with and without the addition of standard solutions at each concentration level of calcium and magnesium to obtain the calibration curve.

# 5.1.2.6 Calculation and Expression

The contents of calcium and magnesium are calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Calcium or Magnesium (mg/kg) =  $\frac{\text{Amount of calcium or magnesium obtained }(\mu g) \times f}{\text{Amount of sample salt used }(g)} \times 20$ 

where f is the factor of the standard stock solution of each component.

## 5.1.2.7 Remarks

(1) In case calcium (10 mg/kg or more) and magnesium (1 mg/kg or more) are to be measured, prepare the sample solution in accordance with item 4.1 and analyze it directly. In this case, add 2 g of sodium chloride to each solution for the calibration graph and measure off stepwise definite volumes of the standard solutions of calcium (0.04 mg/mL) and magnesium (0.02 mg/mL) exactly in the range of 0.5 to 5 mL and from 1 to 10 mL, respectively, and prepare the calibration curves using these solutions.

(2) In case the sample solution contains insoluble matter, filter it with a dried filter paper (No. 5C). In this case, discard the first 5 mL of the filtrate and use the rest for the analysis.

(3) In case the nebulizer is plugged while spraying the sample solution, filter the sample solution before use.(4) When the high order spectral lines can be used in the apparatus, they may be used for the analysis. In the selection of the wavelength for an element, make sure that there is no interference from closely located spectral lines of other elements.

(5) The background correction must always be done to obtain the accurate emission intensity.

(6) Adjust the concentrations of the standard solutions for the calibration curve in accordance with the sensitivity of the apparatus for the element to be determined and its content in the sample solution.

# 5.2 Sulfate Ion (Ion chromatography)

# 5.2.1 Principle

The sample salt is dissolved in water and the sulfate ion is determined by ion chromatography. This method is applicable when the content of the sulfate ion is 20 to 200 mg/kg.

# 5.2.2 Apparatus

(1) An ion chromatograph: the one specified in item 4.6.2.2.

## 5.2.3 Reagents

(1) Water: the one specified in item 4.6.2.3(1).

- (2) Eluent: the one specified in item 4.6.2.3(2).
- (3) Regenerant: the one specified in item 4.6.2.3(3).
- (4) Standard solution of sulfate ion (10  $\mu$ g/mL)

Measure off exactly 5 mL of the standard stock solution of sulfate ion (1 mg/mL) prepared in accordance with item 4.6.1.3(4), transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

(5) Standard solution of sulfate ion (1  $\mu$ g/mL)

Measure off exactly 10 mL of the standard solution of sulfate ion (10  $\mu$ g/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with water.

#### 5.2.4 Procedure

(1) Measure off exactly 5 mL of the sample solution prepared in accordance with item 4.1, transfer it to a 200-mL measuring flask, dilute it to the mark with water to obtain the sample solution for the sulfate ion (concentration of sample salt: 0.05 %) <sup>(1)</sup>.

(2) Regulate the apparatus in accordance with its manual, inject the sample solution for the sulfate ion and obtain the chromatogram.<sup>(1)</sup> Read out the height or the area of the peak corresponding to the sulfate ion.
(3) Determine the amount of the sulfate ion (μg) from the calibration curve prepared separately.

#### 5.2.5 Preparation of Calibration Curve

Measure off stepwise definite volumes of the standard solution of sulfate ion  $(1 \ \mu g/mL)$  exactly within the range of 1 to 10 mL<sup>(1)</sup>, transfer each to a 100-mL measuring flask, and dilute it to the mark with water. Carry out item 5.2.4(2) on each solution and determine the relationship between the amount of the sulfate ion ( $\mu g$ ) and the peak height or the peak area to obtain the calibration curve.

## 5.2.6 Calculation and Expression

The content of the sulfate ion (mg/kg) is calculated on the basis of the following equation <sup>(2)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

Sulfate ion (mg/kg) = 
$$\frac{\text{Amount of sulfate ion obtained }(\mu g)}{\text{Amount of sample salt used }(g)} \times 200 \times f_{so4}$$

# 5.2.7 Remarks

(1) Refer to items 4.6.2.7(1) to (7).

(2) The equation in item 5.2.6 is obtained by rearranging the following equation:

Sulfate ion (mg/kg) = 
$$\frac{\text{Amount of sulfate ion obtained } (\mu g) \times \frac{1}{1000 \times 100} \times f_{S04}}{\frac{\text{Amount of sample salt used } (g)}{1000 \times 500} \times \frac{5}{200}}$$

(38)

## 5.3 Potassium

- 5.3.1 Potassium (Atomic absorption spectrometry)
- 5.3.1.1 Principle

The sample solution is sprayed in the flame of acetylene-air and the atomic absorption of potassium is measured at the wavelength of 766.5 or 769.8 nm to determine potassium. This method is applicable when the content of potassium is 10 to 250 mg/kg.

- 5.3.1.2 Apparatus<sup>(1)</sup>
- (1) An atomic absorption spectrometer
  - The apparatus is regulated in accordance with its manual. Acetylene is used for the fuel.
- (2) A potassium hollow cathode lamp

## 5.3.1.3 Reagents

- (1) Standard stock solution of potassium (1 mg/mL): the one specified in item 4.7.3(1).
- (2) Standard solution of potassium (10  $\mu$ g/mL)

Measure off exactly 5 mL of the standard stock solution of potassium (1 mg/mL), transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

## (3) Cesium chloride solution (20 mg-Cs/mL)

Weigh out 6.4 g of cesium chloride (CsCl), dissolve it in water, transfer the solution to a 250-mL measuring flask and dilute it to the mark with water.

# 5.3.1.4 Procedure

(1) Measure off exactly  $10 \text{ mL}^{(2)}$  of the sample solution prepared in accordance with item 4.1, transfer it to a 100-mL measuring flask, add 5 mL of cesium chloride solution, dilute the solution to the mark with water to obtain the sample solution for potassium.

(2) After regulating the atomic absorption spectrometer, adjust the wavelength to 766.5 or 769.8 nm. Spray the sample solution for potassium to the flame of acetylene-air, read out the indicated value (absorbance) of the apparatus, and obtain the amount of potassium ( $\mu$ g) from the calibration curve prepared separately.

## 5.3.1.5 Preparation of Calibration Curve

(1) Prepared the No.1 to 6 standard solutions for the calibration curve specified in Table 6 as follows: Measure off definite volumes of the standard solution of potassium (10  $\mu$ g/mL) and cesium chloride solution (20 mg-Cs/mL) specified in Table 6, transfer them to a 100-mL measuring flask, and dilute them to the mark with water.

(2) Spray the No.1 to 6 standard solutions for the calibration curve, and read the indicated values. Determine the relationship between the amount of potassium ( $\mu$ g) and the indicated value (absorbance) to obtain the calibration curve. Prepare the calibration curve every time when the sample solution for potassium is analyzed.

Solution	Volume of standard	Volume of cesium chloride	Amount of
number	solution of potassium	solution (20 mg-Cs/mL)	potassium (µg)
	(10 µg/mL) added(mL)	added (mL)	
1	0	5.0	0
2	1.0	5.0	10
3	2.0	5.0	20
4	3.0	5.0	30
5	4.0	5.0	40
6	5.0	5.0	50

Table 6Standard solutions for the calibration curve

## 5.3.1.6 Calculation and Expression

The content of potassium (mg/kg) is calculated on the basis of the following equation <sup>(3)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

Potassium (mg/kg) = 
$$\frac{\text{Amount of potassium obtained }(\mu g) \times 50 \times f_{\kappa}}{\text{Amount of sample salt used }(g)}$$

# 5.3.1.7 Remarks

(1) To minimize contamination from glass apparatus and tools used for the analysis, it is recommended they be rinsed with dilute acid before use.

(2) In case the content of potassium is over the upper limit of the application range, decrease the volume of the sample solution measured off.

(3) The equation in item 5.3.1.6 is obtained by rearranging the following equation:

Potassium (mg/kg) = 
$$\frac{\frac{\text{Amount of potassium obtained }(\mu g)}{1000} \times f_{\kappa}}{\frac{\text{Amount of sample salt used }(g)}{1000} \times \frac{10}{500}}$$

# 5.3.2 Potassium (Flame photometry)

5.3.2.1 Principle

The sample solution is sprayed into the flame of acetylene-air and the emission intensity of the bright line of potassium at the wavelength of 766.5 or 769.8 nm is measured to determine potassium. This method is applicable when the content of potassium is 10 to 100 mg/kg.

# 5.3.2.2 Apparatus

(1) An atomic absorption spectrometer

The apparatus is regulated according to its manual. Acetylene is used for the fuel.

5.3.2.3 Reagents

- (1) Standard stock solution of potassium (1 mg/mL): the one specified in item 4.7.3(1).
- (2) Standard solution of potassium (10 µg/mL)

Measure off exactly 5 mL of the standard stock solution of potassium (1 mg/mL), transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

(3) Standard reagent of sodium chloride (JIS K 8005)

5.3.2.4 Procedure<sup>(1)</sup>

(1) Weigh out approximate 1.0 g of the sample salt exactly, dissolve it with water, transfer the solution to a 100-mL measuring flask, and dilute it to the mark with water to obtain the sample solution.

(2) Regulate the apparatus so as to be used in the flame photometric mode, and adjust the wavelength at 766.5 or 769.8 nm. Spray the sample solution to the flame of acetylene-air, read out the indicated value on the scale, and obtain the amount of potassium ( $\mu$ g) from the calibration curve prepared separately.

5.3.2.5 Preparation of Calibration Curve

(1) Prepare the No. 1 to 7 standard solutions for the calibration curve specified in Table 7 as follows: Weigh out 1.0 g of sodium chloride, dissolve it in water and transfer it to a 100-mL measuring flask. Measure off the definite volume of the standard solution of potassium (10  $\mu$ g/mL) specified in Table 7, add it to the measuring flask containing sodium chloride solution, and dilute the solution to the mark with water.

Solution	Volume of standard	Amount of	Amount of
number	solution of potassium (10	sodium chloride	potassium
	µg/mL) added (mL)	added (g)	(µg)
1	0	1.0	0
2	1.0	1.0	10
3	2.0	1.0	20
4	4.0	1.0	40
5	6.0	1.0	60
6	8.0	1.0	80
7	10.0	1.0	100

Table 7Standard solutions for calibration curve

(2) Spray the No. 1 to 7 standard solutions for the calibration curve successively in accordance with item 5.3.2.4(2), and read out the indicated values. Calculate the true indicated values of No. 2 to 7 by subtracting the indicated value of No. 1 from those of No.2 to 7. Determine the relationship between the amount of potassium ( $\mu$ g) and the true indicated value (absorbance) to obtain the calibration curve. Prepare the calibration curve every time when the sample solution is analyzed.

## 5.3.2.6 Calculation and Expression

The content of potassium (mg/kg) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Potassium (mg/kg) = 
$$\frac{\text{Amount of potassium obtained (}\mu g)}{\text{Amount of sample salt used (g)}} \times f_{\text{K}}$$

5.3.2.7 Remarks

(1) To minimize contamination from glass apparatus and tools used for the analysis, it is recommended they be rinsed with dilute acid before use.

# 6. PARTICULAR TRACE COMPONENTS

6.1 Heavy Metals (Nephelometry with sodium sulfide)

# 6.1.1 Principle

The sample salt is dissolved in nitric acid, neutralized, acidified slightly, and sodium sulfide is added to the resultant solution for coloration. Whether the content of heavy metals in this solution is within the criterion or not is judged by comparing its color with the color of the solution containing a known amount of the lead ion treated in the same manner.

# 6.1.2 Apparatus

(1) Test tubes with ground-in stoppers

Test tubes with ground-in stoppers of about 1.5 cm in inner diameter, about 20 cm in length and with graduations in every 5 mL shall be used. Use only those tubes whose water levels are within the  $100 \pm 2$  % range of the average of the water levels of a set of test tubes when the same volume of water is placed in every tube.

6.1.3 Reagents

- (1) Nitric acid (1+13)
- (2) *p*-Nitrophenol solution (0.25 %)

Dissolve 0.25 g of *p*-Nitrophenol (p-C<sub>6</sub>H<sub>4</sub>OH·NO<sub>2</sub>) in water, and dilute the solution to 100 mL with water.

(3) Hydroxylammonium chloride solution (2 %)

Dissolve 2 g of hydroxylammonium chloride [(NH<sub>3</sub>OH)Cl] (hydroxylamine hydrochloride) in water and dilute the solution to 100 mL with water. Prepare this solution every time when it is used.

- (4) Acetic acid (1+20)
- (5) Sodium sulfide solution

Dissolve 5 g of sodium sulfide nonahydrate ( $Na_2S \cdot 9H_2O$ ) in mixed solution of 10 mL of water and 30 mL of glycerol and transfer the solution to a brown-colored bottle. Prepare this solution every time when it is used.

(6) Standard stock solution of lead (0.1 mg/mL)

Weigh out exactly 0.160 g of lead nitrate  $[Pb(NO_3)_2]$ , dissolve it in 25 mL of nitric acid (1+2), transfer the solution to a 1-L measuring flask, and dilute it to the mark with water.

(7) Standard solution of lead (0.01 mg/mL)

Measure off exactly 10 mL of the standard stock solution of lead (0.1 mg/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with water. Prepare this solution every time when it is used.

(8) Sodium hydroxide solution (8%)

Dissolve 80 g of sodium hydroxide (NaOH) in water and dilute the solution to 1 L with water. The factor,  $f_{NaOH}$ , of this solution is determined as follows: Measure off exactly 10 mL of the same nitric acid (1+13) used in the preparation of the sample solution in item 6.1.4(1), transfer it to a 200-mL flask for titration, add one drop of p-nitrophenol solution (0.25 %), and titrate the solution with sodium hydroxide solution (8 %) (titration volume: "*a*" mL) until the color of the solution changes to faint yellow. The factor is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

 $f_{\text{NSOH}} = 5/a$  (Titration volume of sodium hydroxide solution, mL)

Calculate the volume of sodium hydroxide solution (8 %), "b" mL, required in item 6.1.4(2) on the basis of the following equation:

$$b (\text{mL}) = 3.8/f_{\text{NaOH}}$$

6.1.4 Procedure<sup>(1)</sup>

(1) Weigh out 10 g of sample salt exactly, transfer it to a 100-mL beaker, add 40 mL of nitric acid (1+13) to dissolve it, and boil the solution gently for about 5 minutes. After cooling it, transfer the solution to a 50 mL-measuring flask and dilute it to the mark with water to obtain the sample solution  $^{(2)}$ .

(2) Measure off exactly 10 mL of the sample solution, transfer it to a 100-mL beaker, and add a drop of p-nitrophenol solution (0.25 %) and b mL of sodium hydroxide solution (8 %). Add 0.5 mL of hydroxylammonium chloride solution (2 %), stir the solution, and allow it to stand for 20 minutes.

(3) Then <sup>(3)</sup>, while stirring, add sodium hydroxide solution (8 %) carefully drop by drop until the color of the solution changes to faint yellow. After neutralizing properly, transfer the solution to a test tube with a ground-in stopper.

(4) Add 2.0 mL of acetic acid (1+20) to the test tube and dilute the solution to 20 mL with water. Add one drop of sodium sulfide solution and allow the solution to stand for 10 minutes after mixing thoroughly.(5) Compare the color of the solution with that of the standard solution for comparison treated in parallel.

# 6.1.5 Standard Solution for Comparison

Measure off exactly 5 mL of the sample solution and L/10 mL of the standard solution of lead (0.01 mg/mL) where L is the limiting content of heavy metals in mg/kg, and transfer them to a 100-mL beaker. Add 4 mL of nitric acid (1+13) and carry out items 6.1.4(2) to (4) on the solution to develop the color.

# 6.1.6 Expression

When the color of the standard solution for comparison is darker than or equal to that of the sample solution, the content of the heavy metals is within the allowed range.

## 6.1.7 Remarks

(1) Carry out this analysis, avoiding the exposure to the direct sunrays.

(2) When the sample solution is turbid, filter it before use.

(3) When the solution is yellow before neutralization, add nitric acid (1+13) drop by drop until the solution becomes colorless, and carry our item 6.1.4(3).

## 6.2 Bromide Ion (Ion Chromatography)

# 6.2.1 Principle

The sample salt is dissolved in water and the bromide ion is determined by ion chromatography. This method is applicable when the content of the bromide ion is 250 to 2500 mg/kg.

# 6.2.2 Apparatus

#### (1) An ion chromatograph

Use the ion chromatograph specified in item 4.6.2.2(1). The separation column should be capable of separating the bromide ion from other anionic components. An ultraviolet absorption detector <sup>(1)</sup> may be used as the detector.

#### 6.2.3 Reagents

(1) Water: the one specified in item 4.6.2.3(1).

(2) Eluent  $^{(2)}$ : the one specified in item 4.6.2.3(2).

- (3) Regenerant: the one specified in item 4.6.2.3(3).
- (4) Standard stock solution of bromide ion (1 mg/mL)

Dry approximately 2 g of sodium bromide (NaBr) at 110 °C for about 2 hours and allow it to cool in a desiccator. Weigh out approximately 1.3 g of dried sodium bromide exactly, and dissolve it in water. Transfer the solution to a 1-L measuring flask and dilute it to the mark with water. The factor of this solution,  $f_{\rm Br}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Br} = \frac{\text{Amount of potassium bromide used (g)}}{1.288}$$

(5) Standard solution of bromide ion  $(10 \ \mu g/mL)^{(3)}$ 

Measure off exactly 5 mL of the stock solution of bromide ion (1 mg/mL), transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

# 6.2.4 Procedure

(1) Measure off exactly 10 mL of the sample solution prepared in accordance with item 4.1, transfer it to a 500-mL measuring flask, and dilute it to the mark with water to obtain the sample solution for the bromide

ion (concentration of sample salt: 0.04 %)<sup>(3)</sup>.

(2) Regulate the apparatus in accordance with its manual, inject the sample solution for the bromide ion, and obtain the chromatogram  $^{(3),(4)}$ . Read out the height or the area of the peak corresponding to the bromide ion.

(3) Obtain the amount of the bromide ion  $(\mu g)$  from the calibration curve prepared separately.

## 6.2.5 Preparation of Calibration Curve

Measure off stepwise definite volumes of the standard solution of bromide ion (10  $\mu$ g/mL) exactly within the range of 1 to 10 mL, transfer each to a 100-mL measuring flask <sup>(3)</sup>, dilute it to the mark with water. Carry out item 6.2.4(2) on each solution and determine the relationship between the amount of the bromide ion ( $\mu$ g) and the peak height or the peak area to obtain the calibration curve<sup>(3)</sup>.

# 6.2.6 Calculation and Expression

The content of the bromide ion (mg/kg) is calculated on the basis of the following equation <sup>(5)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

Bromide ion (mg/kg) = 
$$\frac{\text{Amount of bromide ion obtained (\mu g)}}{\text{Amount of sample salt used (g)}} \times 250 \times f_{\text{Br}}$$

#### 6.2.7 Remarks

(1) In case the ultraviolet absorption detector is used, adjust the wavelength at around 210 nm. With this detector, the interference from the chloride ion whose peak is located closely to that of the bromide ion in the chromatogram is eliminated. The ultraviolet absorption detector is thus suited for the determination of a small amount of the bromide ion.

(2) Eluent shown here is a representative one. Other eluents may be used as long as the bromide ion is separated from other anionic components.

(3) Refer to items 4.6.2.7(1) to (8) concerning other general remarks. The sulfate ion there should be read the bromide ion.

(4) Make sure in advance that the peak of the chloride ion does not overlap with that of the bromide ion.

(5) The equation in item 6.2.6 is obtained by rearranging the following equation:

Bromide ion (mg/kg) = 
$$\frac{\text{Amout of bromide ion obtained } (\mu g) \times \frac{1}{1000 \times 100} \times f_{\text{Br}}}{\frac{\text{Amount of sample salt used } (g)}{1000} \times \frac{10}{500 \times 500}}$$

# 6.3 Copper

6.3.1 Copper (Diethyldithiocarbamate Absorptiometry)

6.3.1.1 Principle

After the sample salt is dissolved in water, followed by treating with nitric acid, the pH of the resultant solution is adjusted to approximately 9. Sodium diethyldithiocarbamate solution is added to the solution and the absorbance of the yellow copper complex with diethyldithiocarbamate extracted into butyl acetate is measured to determine copper. This method is applicable when the content of the copper is in the range of 0.1 to 4 mg/kg.

## 6.3.1.2 Apparatus

- (1) A photoelectric spectrophotometer or a photoelectric photometer
- (2) Separatory funnels (200- mL)<sup>(1)</sup>

## 6.3.1.3 Reagents

- (1) Nitric acid(1+1)
- (2) *m*-Cresol purple solution (0.1 %)

Dissolve 0.1 g of m-cresol purple in 50 mL of ethanol, and dilute the solution to 100 mL with water.

(3) EDTA solution

Dissolve 5 g of disodium ethylenediaminetetraacetate dihydrate (EDTA) and 20 g of diammonium hydrogencitrate in 80 mL of water, add 5 mL of aqueous ammonia to the solution, and dilute it to 100 mL with water.

(4) Sodium diethyldithiocarbamate solution (0.1 %)

Dissolve 0.1 g of sodium *N*,*N*-diethyldithiocarbamate trihydrate  $[(C_2H_5)_2NCS_2Na \cdot 3H_2O]$  in water, dilute the solution to 100 mL, and store it in a cool and dark place. This solution is stable for one week. (5) Standard stock solution of copper (0.1 mg/mL)<sup>(2)</sup>

Weigh out approximately 0.10 g of copper (Cu) (JIS K 8005) exactly, dissolve it with 20 mL of nitric acid (1+1) with heating, cool the solution, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Cu}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm cu} = \frac{\text{Amount of copper used (g)}}{0.100} \times \frac{\text{Purity of copper used (\%)}}{100}$$

(6) Standard solution of copper (2  $\mu$ g/mL)

Measure off exactly 5 mL of the standard stock solution of copper (0.1 mg/mL) specified in item(5), transfer it to a 250-mL measuring flask, add 5 mL of nitric acid (1+1), and dilute the solution to the mark with water.

(7) Aqueous ammonia (1+1)

(8) Buthyl acetate(CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)

## 6.3.1.4 Procedure

(1) Weigh out 10 g of sample salt exactly, transfer it to a 200-mL beaker, and add approximately 40 mL of water and 10 mL of nitric acid (1+1) to dissolve it. Boil the solution gently for more than 10 minutes<sup>(3)</sup>, and

then cool the solution to room temperature.

(2) After adding 10 mL of EDTA solution and 2 to 3 drops of m-cresol purple solution (0.1 %) to the resultant solution, add aqueous ammonia (1+1) until the color of the solution changes from yellow to purple <sup>(4)</sup>.

(3) Add 10 mL of sodium diethyldithiocarbanate solution (0.1 %) to this solution, transfer the solution in the beaker to a 200-mL separatory funnel. Rinse the inside of the beaker with a small quantity of water, add washing water to the separatory funnel, and finally dilute the solution to approximately 100 mL with water. (4) Add 10 mL of butyl acetate to the separatory funnel and then shake the mixture vigorously for 3 minutes, and allow it to stand until two layers settle out. Then transfer the butyl acetate layer to a 20-mL conical flask into which approximately 1 g of anhydrous sodium sulfate is placed and shake the flask gently to dehydrate the butyl acetate layer<sup>(3)</sup> which is used for the sample solution to determine copper.

(5) Transfer a portion of this solution to an absorption cell, measure the absorbance at the wavelength of 440 nm with butyl acetate as a reference, and determine the amount of copper ( $\mu$ g) from a calibration curve prepared separately.

(6) Prepare the blank solution without the addition of the sample salt and measure the blank value for copper in the same manner as described above, and obtain the (net) amount of copper ( $\mu$ g) by subtracting the blank value from the determined amount of copper.

#### 6.3.1.5 Preparation of Calibration Curve

Measure off stepwise definite volumes of the standard solution of copper (2  $\mu$ g/mL) exactly within the range of 1 to 20 mL, transfer each to a 200-mL beaker, dilute it to approximately 40 mL with water, and add 10 mL of nitric acid (1+1). Carry out the procedure specified in items (2) to (5) and to determine the relationship between the amount of copper ( $\mu$ g/mL) and the absorbance to obtain the calibration curve.

## 6.3.1.6 Calculation and Expression

The content of copper is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Copper (mg/kg) = 
$$\frac{\text{Amount of copper obtained }(\mu g)}{\text{Amount of sample salt used }(g)} \times f_{Cu}$$

# 6.3.1.7 Remarks

(1) Alternatively, separatory funnels (100-mL) can be used. In such case, carry out the procedure specified in item 6.3.1.4 using each half amount of the sample salt, water and reagents described in the procedure.

(2)The standard solution of copper (0.1mg/mL) may be prepared by the following method.

Weigh out 0.393 g of copper(II) sulfate heptahydrate (CuSO<sub>4</sub>  $\cdot$  5H<sub>2</sub>O), dissolve it in water, transfer the solution to a 1-L measuring flask, add 20 mL of nitric acid(1+1), and dilute it to the mark with water.

(3) Pay attention to salt samples containing large amounts of brine components, as insufficient boiling of the solution may not cause the m-cresol purple to change color even in the proper pH region.

(4) A pH meter may be used instead of adding the *m*-cresol purple solution (0.1%) to adjust the solution pH to 9.

(5) The butyl acetate layer may be filtered through a dry filter paper.

6.3.2 Copper (Atomic Absorption Spectrometry)

#### 6.3.2.1 Principle

After the sample salt is dissolved in water, followed by treating with nitric acid, the pH of the resultant solution is adjusted to approximately 4 with aqueous ammonia. APDC solution is added to the resultant solution and the copper-APDC complex formed is extracted into DIBK. The DIBK layer is sprayed into the flame of acetylene-air and the atomic absorption is measured at the wavelength of 324.7 nm for determining copper <sup>(1)</sup>. This method is applicable when the content of copper is in the range of 0.05 to 0.5 mg/kg.

#### 6.3.2.2 Apparatus

- (1) An atomic absorption spectrometer: the one specified in item 5.1.1.2(1).
- (2) A copper hollow cathode lamp
- (3) Separatory funnels (200-mL)

## 6.3.2.3 Reagents

(1) Standard solution of copper (1  $\mu$ g/mL)

Measure off exactly 5 mL of the standard stock solution of coppe(0.1 mg/mL) specified in item 6.3.1.3(5), transfer it to a 500-mL measuring flask, add 10 mL of nitric acid (1+1), and dilute the solution to the mark with water.

(2) Ammonium 1-pyrrolidinecarbodithioate (APDC) solution (2 %)

Dissolve 2 g of ammonium 1-pyrroridinecarbodithioate (APDC) in water, dilute the solution to 100 mL, and transfer the solution to a 200-mL separatory funnel. Add 30 mL of DIBK to the separatory funnel, and then shake the mixture vigorously for approximately 5 minutes, and allow it to stand until the two layers are separated. Use the water layer drained off as the reagent solution of APDC.

(3) Diammonium hydrogeneitrate solution (0.5 mol/L)

Dissolve 56 g of diammonium hydrogencitrate  $[(NH_4)_2HC_6H_5O_7]$  in water, dilute the solution to 500 mL, and transfer the solution to a 1000-mL separatory funnel. Add 10 mL of APDC solution and 30 mL of DIBK to the separatory funnel and then shake the mixture vigorously for approximately 1 minute, and allow it to stand until the two layers are separated. Then discard the DIBK layer. Repeat the same extraction peocedure as described above. Use the water layer drained off is used as the reagent solution.

(4) Aqueous ammonia (1+1)

(5) Nitric acid (1+1)

- (6) 2, 6-dimethyl-4-heptanone [diisobuthylketone (DIBK)] [((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>)<sub>2</sub>CO]
- (7) Methyl orange solution (0.2 %)

Dissolve 0.2 g of methyl orange in 100 mL of water, and store it in a brown-colored bottle.

# 6.3.2.4 Procedure

(1) Weigh out 20 g of sample salt exactly, transfer it to a 200-mL beaker, add 70 mL of water and 10 mL of nitric acid (1+1) to dissolve it, and boil the solution gently for 5 minutes.

(2) After cooling the solution, transfer it into a 200-mL separatory funnel, add 5 mL of diammonium hydrogeneitrate solution (0.5 mol/L) and 2 to 3 drops of methyl orange solution (0.2 %) to it, and then add aqueous ammonia (1+1) until the color of the solution becomes yellow.

(3) Add 5 mL of APDC solution (2 %) and 10 mL of DIBK to the separatory funnel and then shake the mixture vigorously for approximately 5 minutes, and allow it to stand until the two layers are separated. Then drain off the DIBK layer to an appropriate vessel with a ground-in stopper Use the DIBK as the sample solution to determine copper.

(4) After regulating the atomic absorption spectrometer, adjust the wavelength to 324.7 nm for copper. Spray the sample solution (the DIBK in item (3)) into the flame of acetylene-air, and record the indicated value (absorbance) of the apparatus, and determine the amount of copper ( $\mu$ g) from the calibration curve prepared separately.

(5) Prepare the blank solution without the addition of the sample salt and measure the blank value for copper in the same manner as described above, and obtain the (net) amount of copper ( $\mu$ g) by subtracting the blank value from the amount of copper determined in the procedure (4).

## 6.3.2.5 Preparation of Calibration Curve

(1) Measure off stepwise definite volumes of the standard solution of copper (1  $\mu$ g/mL) exactly within the range of 1 to 10 mL and transfer each to a 200-mL beaker. Add 70 mL of water and 10 mL of nitric acid (1+1) to each solution, and carry out the procedures specified in items 6.3.2.4 (2) and (3) to prepare the sample solution for analysis.

(2) Carry out the procedure specified in 6.3.2.4 (4) to determine the relationship between the amount of copper ( $\mu$ g) and the indicated value to obtain the calibration curve.

## 6.3.2.6 Calculation and Expression

The content of copper is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Copper (mg/kg) = 
$$\frac{\text{Amount of copper obtained }(\mu g)}{\text{Amount of sample salt used }(g)} \times f_{Cu}$$

# 6.3.2.7 Remarks

(1) In accordance with the present method, the sample solution can be used commonly to determine cadmium and lead.

# 6.3.3 Copper (ICP-Optical Emission Spectrometry)

# 6.3.3.1 Principle

The sample salt is treated with nitric acid and the resultant solution is sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength of 324.754 nm is

detected with the spectrometer and the emission intensity at this wavelength is measured to determine copper.

## 6.3.3.2 Apparatus

(1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer)<sup>(1)</sup>

The apparatus shall be used with a plasma torch fitted with a nebulizer for high salt concentration. It should be capable of monitoring at two wavelengths in parallel and is regulated in accordance with the manual.

#### 6.3.3.3 Reagents

## (1) Yttrium solution (10 $\mu$ g/mL)

Weigh out 0.318 g of yttrium oxide ( $Y_2O_3$ ), dissolve it with 5 mL of ultra pure nitric acid (JIS K 9901) with heating, cool the solution, transfer it to a 250-mL measuring flask, and dilute it to the mark with water. Measure off exactly 5 mL of the solution, transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

(2) Standard solution of copper (10  $\mu$ g/mL)

Measure off exactly 10 mL of the standard stock solution of copper (0.1 mg/mL) specified in item 6.3.1.3(5), transfer it to a 100-mL measuring flask, add 10 mL of nitric acid (1+1), and dilute the solution to the mark with water.

(3) Sodium chloride: the standard reagent of sodium chloride (NaCl) (JIS K 8005)

(4) Argon gas

(5) Nitric acid (1+1)

# 6.3.3.4 Procedure<sup>(1)</sup>

(1) Weigh out approximately 10 g of the sample salt exactly, dissolve it with 40 mL of water and 10 mL of nitric acid (1+1), and boil the solution for 10 minutes.

(2) Cool the solution, transfer it to a 100-mL measuring flask, add 10 mL of yttrium solution (10  $\mu$ g/mL), and dilute the solution to the mark with water to obtain the sample solution <sup>(2)</sup>.

(3) Regulate the apparatus, spray the sample solution into the plasma torch  $^{(3)}$ , measure the emission intensity at the wavelength of 324.754 nm for copper and that at the wavelength of 371.029 nm for yttrium in parallel  $^{(4),(5)}$ .

(4) Divide the emission intensity of the copper by that of yttrium to obtain the emission intensity ratio, and obtain the amount of copper ( $\mu$ g) from the calibration curve prepared separately.

## 6.3.3.5 Preparation of Calibration Curve

(1) Measure off stepwise definite volumes of the standard solution of copper (10  $\mu$ g/mL) exactly, transfer each to a 100-mL measuring flask, and add 10 mL of nitric acid (1+1), 10 mL of yttrium solution (10  $\mu$ g/mL) and 10 g of sodium chloride to each solution.

(2) After dissolving the sodium chloride completely, dilute each solution to the mark with water. Carry out the procedures specified in items 6.3.3.4(3) and (4) to determine the relationship between the amount of the element ( $\mu$ g) and the emission intensity ratio to obtain the calibration curve.

# 6.3.3.6 Calculation and Expression

The content of copper is calculated on the basis of the following equation compared with the tolerance, and reported in accordance with item 2.6.

Copper (mg/kg) = 
$$\frac{\text{Amount of copper obtained }(\mu g)}{\text{Amount of sample salt used }(g)} \times f_{Cu}$$

6.3.3.7 Remarks

(1) In case the apparatus is incapable of measuring two or more emission intensities in parallel, measure the emission intensities of copper and yttrium sequentially and obtain the emission intensity ratio.

(2) In case the sample solution contains insoluble matter, filter it with a dried filter paper (No.5C). In this case, discard the first 5 mL of the filtrate and use the rest for the analysis.

(3) In case the nebulizer is plugged while spraying the sample solution, filter the sample solution before use.

(4) The background correction must always be done to obtain the accurate emission intensity.

(5) When the high order spectral lines can be used in the apparatus, they may be used for the analysis. In the selection of the wavelength for an element, make sure that there is no interference from closely located spectral lines of other elements.

(6) In case other elements are determined simultaneously, calibration curves are made using mixed standard solutions under the measurement conditions suitable to each element.

(7) Adjust the concentration and the volume of the standard solution used in the preparation of the calibration curve in accordance with the sensitivity of the apparatus for copper.

## 6.4 Cadmium

# 6.4.1 Cadmium (Atomic Absorption Spectrometry)

# 6.4.1.1 Principle

After the sample salt is dissolved in water, followed by treating with nitric acid, the pH of the resultant solution is adjusted to approximately 4 with aqueous ammonia. APDC solution is added to the resultant solution and the cadmium-APDC complex formed is extracted into DIBK. The DIBK is sprayed into the flame of acetylene-air and the atomic absorption is measured at the wavelength of 228.8 nm for determining cadmium <sup>(1)</sup>. This method is applicable when the content of cadmium is in the range of 0.02 to 0.2 mg/kg.

# 6.4.1.2 Apparatus

- (1) An atomic absorption spectrometer: the one specified in item 5.1.1.2(1).
- (2) A cadmium hollow cathode lamp
- (3) Separatory funnels (200 mL)

# 6.4.1.3 Reagents

(1) Standard stock solution of cadmium (0.1 mg/mL)

Weigh out approximately 0.10 g of cadmium (Cd) (purity: 99.9 % or better) exactly, dissolve it in 25

mL of nitric acid (1+1) with heating. Boil the solution to expel nitrogen oxides, cool it, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Cd}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{cd} = \frac{\text{Amount of cadmium used (g)}}{0.100} \times \frac{\text{Purity of cadmium used (\%)}}{100}$$

(2) Standard solution of cadmium  $(1 \mu g/mL)$ 

Measure off exactly 5 mL of the standard stock solution of cadmium (0.1 mg/mL) specified in item (1), transfer it to a 500-mL measuring flask, add 10 mL of nitric acid (1+1), and dilute the solution to the mark with water.

- (3) Ammonium 1-pyrrolidinecarbodithioate (APDC) solution (2%): the one specified in item 6.3.2.3(2)
- (4) Diammonium hydrogencitrate solution (0.5 mol/L): the one specified in item6.3.2.3(3)
- (5) Aqueous ammonia (1+1)

(6) Nitric acid (1+1)

(7) 2,6-dimethyl-4-heptanone[diisobuthylketone(DIBK)][((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>)<sub>2</sub>CO]

(8) Methyl orange solution (0.2 %): the one specified in item 6.3.2.3(7)

6.4.1.4 Procedure

(1) Carry out the procedures specified in items 6.3.2.4(1) to (3) and prepare the sample solution.

(2) After regulating the atomic absorption spectrometer, adjust the wavelength to 228.8 nm for cadmium. Spray the sample solution (the DIBK specified in item (3)) into the flame of acetylene-air and record the indicated value (absorbance) of the apparatus, and determine the amount of cadmium ( $\mu$ g) from the calibration curve prepared separately.

(3) Prepare the blank solution without the addition of the sample salt and measure the blank value for cadmium in the same manner as described above, and obtain the (net) amount of cadmium ( $\mu$ g) by subtracting the blank value from the amount of cadmium determined in the procedure (2).

# 6.4.1.5 Preparation of Calibration Curve

(1) Measure off stepwise definite volumes of the standard solution of cadmium (1  $\mu$ g/mL) exactly within the range of 1 to 10 mL and transfer each to a 200-mL beaker. After adding 70 mL of water and 10 mL of nitric acid (1+1) to each solution, carry out the procedure specified in items 6.3.2.4(2) and (3) to prepare the sample solution for analysis.

(2) Carry out the procedure specified in item (2) to determine the relationship between the amount of cadmium ( $\mu$ g) and the indicated value to obtain the calibration curve.

# 6.4.1.6 Calculation and Expression

The content of cadmium is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Cadmium (mg/kg) = 
$$\frac{\text{Amount of cadmium obtained (}\mu g)}{\text{Amount of sample salt used (}g)} \times f_{Cd}$$

6.4.1.7 Remarks

(1) In accordance with the present method, the same sample solution can be used commonly to determine copper and lead.

# 6.4.2 Cadmium (ICP-Optical Emission Spectrometry)

6.4.2.1 Principle

The sample salt is treated with nitric acid and the resultant solution is sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength of 214.438 nm is detected with the spectrometer and the emission intensity at this wavelength is measured to determine cadmium.

6.4.2.2 Apparatus

(1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer): the one specified in item 6.3.3.2(1).

6.4.2.3 Reagents

(1) Yttrium solution (10  $\mu$ g/mL): the one specified in item 6.3.3.3(1)

(2) Standard solution of cadmium(1  $\mu$ g/mL): the one specified in item 6.4.1.3(2)

(3) Sodium chloride: the standard reagent of sodium chloride (NaCl) (JIS K 8005)

(4) Argon gas

(5) Nitric acid (1+1)

6.4.2.4 Procedure

(1) Carry out the procedure specified in items 6.3.3.4(1) and (2) and prepare the sample solution for analysis. (2) Regulate the apparatus, spray the sample solution in the plasma torch, measure the emission intensity at the wavelength of 214.438 nm for cadmium and that at the wavelength of 371.029 nm for yttrium in parallel. (3) Divide the emission intensity of the cadmium by that of yttrium to obtain the emission intensity ratio, and obtain the amount of cadmium ( $\mu$ g) from the calibration curve prepared separately.

6.4.2.5 Preparation of Calibration Curve<sup>(1)</sup>

(1) Measure off stepwise definite volumes of the standard solution of cadmium, transfer each of them to a 100-mL measuring flask, and add 10 mL of nitric acid (1+1), 10 mL of yttrium solution (10  $\mu$ g/mL) and 10 g of sodium chloride to each solution.

(2) After dissolving the sodium chloride completely, dilute each solution to the mark with water. Carry out the procedure specified in items 6.4.2.4(2) and (3) to determine the relationship between the amount of the cadmium ( $\mu$ g) and the emission intensity ratio to obtain the calibration curve.

## 6.4.2.6 Calculation and Expression

The content of cadmium is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Cadmium (mg/kg) = 
$$\frac{\text{Amount of cadmium obtained (}\mu g)}{\text{Amount of sample salt used (}g)} \times f_{Ca}$$

6.4.2.7 Remarks

(1) Refer to items 6.3.3.7 concerning general remarks for measurements. However, substitute the element to be determined from copper to cadmium.

6.5 Mercury (Reduction and Vaporization/Atomic Absorption Spectrometry)

# 6.5.1 Principle

The sample salt is dissolved in water and the resultant solution is treated with potassium chlorate. Then the mercury (II) is reduced by tin (II) chloride to generate Hg vapor and the atomic absorption is measured at the wavelength of 253.7 nm to determine mercury. This method is applicable when the content of mercury is in the range of 0.1 to 1.25 mg/kg.

6.5.2 Apparatus

- (1) Atomic absorption spectrometer or atomic absorption spectrometer exclusively for mercury
- (2) A mercury vapor generator by the reduction (used jointly with an atomic absorption spectrometer) <sup>(1)</sup> Examples of the apparatus are shown in Figs. 3 and 4.



Fig. 3 An example for the configuration of a closed circuit system

- A :Reduction vessel
- B :Drying tube
- C :Flow meter
- $D \quad : Absorption \ cell \\$
- E :Air pump



Fig. 4 An example of the configuration of an open type air delivering system

- F :Recorder
- G : Hg hollow cathode lamp
- H :Atomic absorption detector
- I :Apparatus for removing Hg

(3) A mercury hollow cathode lamp or Hg-lamp

(4) Reduction vessel: 300 to 350 mL-glass bottle or conical flask marked at 250 mL

(5) An absorption cell: quartz, glass or plastic cell (quartz-windowed at both ends with an optical path length of 100 to 300 mm).

(6) An air pump: diaphragm pump with an air flow rate capacity of 0.3 to 3 L/minute.

In case the components of the pump in contact with Hg vapor are made of metal, coat with collodion on surfaces of components.

(7) A flow meter: with a capacity to measure a flow rate of 0.5 to 5 L/min

(8) A drying tube: A drying tube or U-shaped tube packed with granular magnesium perchlorate or calcium chloride is used, but a cold trap can be substituted. The drying tube is not necessary when the temperature inside the absorption cell is maintained at a temperature of approximately 10 °C higher than the ambient temperature by suitable means such as lighting a small lamp at the port of the absorption cell.

(9) Connecting tube: Use plasticized polyvinyl chloride tubing. (An apparatus for generating mercury vapor by reduction consists of a reduction vessel, absorption cell, air pump, flow meter, drying tube and connecting tube. The apparatus should be regulated in accordance with its operation manual.)

6.5.3 Reagents<sup>(2)</sup>

(1) Standard stock solution of mercury (0.5 mg/mL)

Weigh out approximately 0.34 g of mercury (II) chloride (HgCl<sub>2</sub>) exactly, dissolve it in water, add 5 mL of nitric acid (1+1), transfer it to a 500-mL measuring flask, dilute it to the mark with water, and store the solution in a brown-colored bottle. The solution should not be kept for more than one month. The factor of this solution,  $f_{Hg}$  is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

 $f_{Hg}$  =Amount of mercury(II) chloride used(g)/0.339

(2) Standard solution of mercury (1  $\mu$ g/mL)

Measure off exactly 1 mL of the standard stock solution of mercury (0.5 mg/mL) specified in item (1), transfer it to a 500-mL measuring flask, add 5 mL of nitric acid (1+1), and dilute the solution to the mark with water. Prepare this solution every time when it is used.

(3) Potassium chlorate solution (10 %)

Dissolve 10 g of potassium chlorate in water, and dilute the solution to 100 mL with water.

(4) Hydroxylammonium chloride solution (10 %)

Dissolve 10 g of hydroxylammonium chloride [(NH<sub>3</sub>OH)Cl] in water and dilute the solution to 100 mL with water. Prepare this solution every time when it is used.

(5) Tin(II) chloride solution

Dissolve 10 g of tin(II) chloride dihydrate( $SnCl_2 \cdot 2H_2O$ ) in 60 mL of sulfuric acid (1+20) with heating. After cooling the solution, dilute the solution to 100 mL with water, transfer it into a brown-colored bottle into which 2 to 3 granules of tin are added inside, and store it in a dark place. In case purification of the solution is needed, pass  $N_2$  gas through the solution. The solution should not be kept for more than one week.

(6) Hydrochloric acid(1+1)

## 6.5.4 Procedure (3), (4)

(1) Weigh out 10 g of sample salt exactly, transfer it to a 200-mL beaker, and dissolve it with the addition of approximately 60 mL of water.

(2) Add 4 mL of hydrochloric acid (1+1) and 3 mL of potassium chlorate solution (10 %) and heat the solution at approximately 90 °C for 30 minutes. After cooling the solution, transfer it to a 100-mL measuring flask, and dilute the solution to the mark with water.

(3) Measure off 20 mL of this solution exactly, transfer it to the 300 to 350-mL glass bottle or conical flask used for the reduction, add 20 mL of hydroxylammonium chloride solution (10 %) and then dilute the solution to the mark with water<sup>(5)</sup>. Set up a system to pass the gas through the solution together with this procedure.
(4) Add tin (II) chloride solution quickly, and then start the air pump to circulate air at the optimal flow rate determined previously.

(5) Record the indicated value (absorbance) at the wavelength of 253.7 nm, and determine the amount of mercury ( $\mu$ g) from a calibration curve prepared separately.

(6) Next, turn the bypass cock and continue to supply air until the indicated value returns to the original (former) one.

(7) Prepare the blank solution without the addition of the sample salt and measure the blank value for mercury in the same manner as described above, and obtain the (net) amount of mercury ( $\mu$ g) by subtracting the blank value from the amount of mercury determined in the procedure.

# 6.5.5 Preparation of Calibration Curve

Measure off stepwise definite volumes of the standard solution of mercury (1  $\mu$ g/mL) exactly within the range of 2 to 25 mL and transfer each to a 200-mL beaker. After adding 50 mL of water, carry out the procedure specified in items 6.5.4 (2) to (6) to determine the relationship between the amount of mercury ( $\mu$ g) and the indicated value to obtain the calibration curve.

Prepare the calibration curve every time when the sample is analyzed.

# 6.5.6 Calculation and Expression

The content of mercury is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Mercury (mg/kg) = 
$$\frac{\text{Amount of mercury obtained }(\mu g)}{\text{Amount of sample salt used }(g)} \times f_{Hg}$$

# 6.5.7 Remarks

(1) To remove mercury from the gas used for measurements on release into the atmosphere, use either a gaswashing bottle in which 100 mL of sulfuric acid (1+4) containing potassium permanganate is placed, or a (2) Reagents that contain less mercury such as those for atomic absorption spectrometry shall be used.

(3) In case the sample salt contains no organic matter, 6.5.4 procedures (1) to (3) may be ignored and the procedure modified as follows. Weigh out 10 g of sample salt exactly, transfer it to the glass bottle (300 to 350 mL) or conical flask (300 to 350 mL) used for the reduction, dissolve it in water, and add 4 mL of hydrochloric acid (1+1). Add water to make the volume up to 250 mL and then carry out procedures (4) to (7).

(4) Instead of atomic absorption spectrometry, ICP-Optical Emission Spectrometry may be used to determine mercury. After treatment of sample salt in accordance with 6.5.4 in items (1) and (2), measure off 25 mL of the solution exactly, transfer it to a 100-mL beaker, add 25 mL of hydroxylammonium chloride solution (10 %) and then stir the solution. Using this solution as the sample solution, carry out the procedure as for arsenic (Hydride generation / ICP-Optical Emission Spectrometry) specified in item 6.7.2.4(3) and determine the amount of mercury ( $\mu$ g). The solutions for a calibration curve shall be prepared so that the same amount of sodium chloride as that of sample salt is used.

(5) When an atomic absorption spectrometer exclusively for mercury is used, measure off exactly 20 mL of the solution obtained in item 6.5.4 (2), and transfer it to a measuring flask (250 mL). Then, add 20 mL of hydroxylammonium chloride solution (10%), and dilute the solution to the mark with water. Measure off an appropriate volume of this solution in accordance with the conditions of the apparatus for mercury, and carry out procedures after item 6.5.4 (4).

6.6 Lead

6.6.1 Lead (Atomic Absorption Spectrometry)

6.6.1.1 Principle

After the sample salt is dissolved in water, followed by treating with nitric acid, the pH of the resultant solution is adjusted to approximately 4 with aqueous ammonia. APDC solution is added to the resultant solution and the lead-APDC complex formed is extracted into DIBK. The DIBK containing the lead complex is sprayed into the flame of acetylene-air and the atomic absorption is measured at the wavelength of 283.3 nm for determining lead <sup>(1)</sup>. This method is applicable when the content of lead is in the range of 0.5 to 5.0 mg/kg.

# 6.6.1.2 Apparatus

- (1) An atomic absorption spectrometer: the one specified in item 5.1.1.2(1).
- (2) A lead hollow cathode lamp
- (3) Separatory funnels (200-mL)

# 6.6.1.3 Reagents

(1) Standard stock solution of lead (0.1 mg/mL)

Weigh out approximately 0.1 g of lead (Pb) (purity: 99.9 % or better) exactly, dissolve it with 25 mL of

nitric acid (1+1) with heating. Boil the solution to remove nitrogen oxides, cool it, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Pb}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Pb} = \frac{\text{Amount of lead used (g)}}{0.100} \times \frac{\text{Purity of lead used (\%)}}{100}$$

(2) Standard solution of lead (50  $\mu$ g/mL)

Measure off exactly 50 mL of the standard stock solution of lead (0.1 mg/mL) specified in item (1), transfer it to a 100-mL measuring flask, add 10 mL of nitric acid (1+1), and dilute the solution to the mark with water.

- (3) Ammonium 1-pyrrolidinecarbodithioate (APDC) solution (2%): the one specified in item 6.3.2.3(2)
- (4) Diammonium hydrogeneitrate solution (0.5 mol/L): the one specified in item 6.3.2.3(3)
- (5) Aqueous ammonia (1+1)

(6) Nitric acid (1+1)

(7) 2, 6-dimethyl-4-heptanone [diisobuthylketone(DIBK)] [((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>)<sub>2</sub>CO]

(8) Methyl orange solution (0.2 %): the one specified in item 6.3.2.3(7).

6.6.1.4 Procedure

(1) Carry out the procedure specified in items 6.3.2.4(1) to (3) and prepare the sample solution.

(2) After regulating the atomic absorption spectrometer, adjust the wavelength to 283.3 nm for cadmium. Spray the sample solution (the DIBK specified in item (3)) into the flame of acetylene-air and record the indicated value (absorbance) of the apparatus, and determine the amount of lead ( $\mu$ g) from a calibration curve prepared separately.

(3) Prepare the blank solution without the addition of the sample salt and measure the blank value for lead in the same manner as described above, and obtain the (net) amount of lead ( $\mu$ g) by subtracting the blank value from the amount of lead determined in the procedure.

## 6.6.1.5 Preparation of Calibration Curve

(1) Measure off stepwise definite volumes of the standard solution of lead (50  $\mu$ g/ mL) exactly within the range of 1 to 10 mL and transfer each to a 200- mL beaker. After adding 70 mL of water and 10 mL of nitric acid (1+1) to each solution, carry out the procedure specified in items 6.3.2.4(2) and (3) to prepare the sample solution for analysis.

(2) Carry out the procedure specified in item 6.6.1.4(2) to determine the relationship between the amount of lead (µg) and the indicated value to obtain the calibration curve.

# 6.6.1.6 Calculation and Expression

The content of lead is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Lead (mg/kg) = 
$$\frac{\text{Amount of lead obtained (\mug)}}{\text{Amount of sample salt used (g)}} \times f_{Pl}$$

6.6.1.7 Remarks

(1) In accordance with the present method, the same sample solution can be used commonly to determine copper and cadmium.

# 6.6.2 Lead (ICP-Optical Emission Spectrometry)

6.6.2.1 Principle

The sample salt is treated with nitric acid and the resultant solution is sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength of 220.351 nm is detected with the spectrometer and the emission intensity at this wavelength is measured to determine lead.

# 6.6.2.2 Apparatus

(1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer): the one specified in item 6.3.3.2(1).

6.6.2.3 Reagents

(1) Yttrium solution (10  $\mu$ g/mL): the one specified in item 6.3.3.3(1).

(2) Standard solution of lead (50  $\mu$ g/mL): the one specified in item 6.6.1.3(2).

(3) Sodium chloride: the standard reagent of sodium chloride (NaCl) (JIS K 8005)

(4) Argon gas

(5) Nitric acid (1+1)

#### 6.6.2.4 Procedure <sup>(1), (2)</sup>

(1) Carry out the procedure specified in items 6.3.3.4(1) and (2) and prepare the sample solution.

(2) Regulate the apparatus, spray the sample solution into the plasma torch, measure the emission intensity at the wavelength of 220.351 nm for lead and that at the wavelength of 371.029 nm for yttrium in parallel.
(3) Divide the emission intensity of the lead by that of yttrium to obtain the emission intensity ratio, and obtain the amount of lead (μg) from the calibration curve prepared separately.

6.6.2.5 Preparation of Calibration Curve<sup>(1)</sup>

(1) Measure off stepwise definite volumes of the standard solution of lead, transfer each of them to a 100-mL measuring flask, and add 10 mL of nitric acid (1+1), 10 mL of yttrium solution (10  $\mu$ g/mL) and 10 g of sodium chloride to each solution.

(2) After dissolving the sodium chloride completely, dilute each solution to the mark with water. Carry out the procedures specified in items 6.6.2.4(2) and (3) to determine the relationship between the amount of the lead ( $\mu$ g) and the emission intensity ratio to obtain the calibration curve.

## 6.6.2.6 Calculation and Expression

The content of lead is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Lead (mg/kg) = 
$$\frac{\text{Amount of lead obtained (\mu g)}}{\text{Amount of sample salt used (g)}} \times f_{Pb}$$

## 6.6.2.7 Remarks

(1) Refer to items 6.3.3.7 concerning general remarks for measurements. However, substitute the element to be determined from copper to lead.

(2) The hydride technique may be used when hydride generation apparatus can be used in the measurement of optical emission. In this case, yttrium solution is omitted in the preparation of the sample solution.

# 6.7 Arsenic

# 6.7.1 Arsenic (Silver Diethyldithiocarbamate Absorptiometry)

# 6.7.1.1 Principle

The sample salt is dissolved in water and the arsenic hydride generated by the reduction of arsenic is absorbed in the silver diethyldithiocarbamate-pyridine solution to yield a reddish purple compound. The absorbance of this compound is measured to determine arsenic. This method is applicable when the content of arsenic is in the range of 0.2 to 1 mg/kg.

#### 6.7.1.2 Apparatus

# (1) An arsenic hydride generator

An example of an arsenic hydride (arsine gas) generator is shown in Fig.5.

(2) A photoelectric spectrophotometer or a photoelectric photometer



- A: Conical flask for generating arsenic hydride
- B: Delivery tube
- b: Glass fiber or absorbent cotton soaked with 10% lead acetate solution (squeeze to remove excess lead acetate solution)
- C: Absorbing tube for arsenic hydride
- D: Rubber stopper

Fig. 5 Arsenic hydride generator (Cf. "Testing methods for industrial water" JIS K 0102-98, by the Japanese Standards Association)

#### 6.7.1.3 Reagents (1)

(1) Standard stock solution of arsenic (0.1 mg/mL)

Weigh out approximately 0.13 g diarsenic trioxide (As<sub>2</sub>O<sub>3</sub>) (JIS K 8005) exactly, dissolve it in 2.5 mL of sodium hydroxide solution(4 %), transfer the solution to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{As}$  is calculated down to 3 places of decimals and rounded off to 2 places of decimals on the basis of the following equation:

$$f_{As} = \frac{\text{Amount of diarsenic trioxide (g)}}{0.132}$$

(2) Standard solution of arsenic  $(2 \mu g/mL)$ 

Measure off exactly 2 mL of the standard stock solution of arsenic (0.1 mg/mL)(1), transfer it to a 100mL measuring flask, and dilute the solution to the mark with water. Prepare this solution every time when it is used.

(3) Potassium iodide solution (20 %)

Dissolve 20 g of potassium iodide (KI) in water, dilute the solution to 100 mL with water, and transfer it to a brown-colored bottle. Store the solution in a dark place.

(4) Tin(II) chloride solution

Dissolve 40 g of tin (II) chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O) in 75 mL of hydrochloric acid with heating. After cooling the solution, dilute the solution to 100 mL with water, transfer and store it in a brown-colored bottle into which 2 to 3 granules of tin are added.

(5) Zinc metal: the reagent for analysis of arsenic (JIS K 8012) (arenaceous).

(6) Lead acetate solution (10 %) (for soaking the absorbent cotton or glass fiber)

Weigh out 10 g of lead acetate trihydride [Pb(CH<sub>3</sub>COO)<sub>2</sub>  $\cdot$  3H<sub>2</sub>O], dissolve it in 100 mL of water with the addition of 2 drops of acetic acid.

(7) Silver diethyldithiocarbamate solution<sup>(2)</sup>

Dissolve 0.25 g of silver *N*,*N*-diethyldithiocarbamate ( $C_5H_{10}AgNS_2$ ) in 100 mL of pyridine, transfer the solution in a brown-colored bottle, and store in a dark place.

(8) Hydrochloric acid: hydrochloric acid for analysis of arsenic (JIS K 8180).

# 6.7.1.4 Procedure

(1) Weigh out 10 g of the sample salt exactly, transfer it to a 300-mL erlenmeyer (conical) flask used for arsenic hydride generation, and add 90 mL of water and 30 mL of hydrochloric acid to dissolve it.

(2) Add 5 mL of potassium iodide solution (20 %) and 5 mL of tin(II) chloride solution to the solution, and allow to stand for 15 minutes.

(3) Add 5 mL of silver diethyldithiocarbamate solution exactly to the absorbing tube for arsenic hydride, and connect the delivery tube with the vessel for hydride generation. After ensureing the airtightness of each port of the apparatus, add 15 g of zinc metal quickly using a funnel into the vessel for hydride generation, and stop up the vessel. Next, place the vessel for hydride generation in a waterbath (approximately 25 °C) and allowed to stand for 60 minutes to develop the color.

(4) Transfer a portion of this solution to an absorption cell, measure the absorbance at the wavelength of 535 nm with water as a reference, and determine the amount of arsenic ( $\mu$ g) from the calibration curve prepared separately.

(5) Prepare the blank solution without the addition of the sample salt and measure the blank value for arsenic in the same manner as described above, and obtain the net amount of arsenic ( $\mu$ g) by subtracting the blank value from the determined amount of arsenic.

## 6.7.1.5 Preparation of Calibration Curve

Measure off stepwise definite volumes of the standard solution of arsenic (2  $\mu$ g/mL) exactly within the range of 1 to 5 mL, transfer each to the 300-mL erlenmeyer (conical) flask for generating arsenic hydride, dilute it to approximately 90 mL with water, and add 30 mL of hydrochloric acid. Carry out the procedure specified in items 6.7.1.4 (2)-(4) to determine the relationship between the amount of arsenic ( $\mu$ g) and the absorbance to obtain the calibration curve.

# 6.7.1.6 Calculation and Expression

The content of the arsenic is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Arsenic (mg/kg) = 
$$\frac{\text{Amount of Arsenic obtained }(\mu g)}{\text{Amount of sample salt used }(g)} \times f_{As}$$

## 6.7.1.7 Remarks

(1) Reagents for atomic absorption spectrometry or those which contain less arsenic shall be used.

(2) Silver diethyldithiocarbamate solution may be prepared alternatively as follows: Add 100 mL of chloroform to 0.25 g of silver diethyldithiocarbamate and 0.1 g of brucine dihydrate( $C_{23}H_{26}N_{24} \cdot 2H_2O$ ) in a mixture and dissolve those with vigorous stirring. In case a loss of chloroform occurs due to volatilization during the dissolution process, supplement with the additional chloroform to make the total volume of the solution 100 mL.

# 6.7.2 Arsenic (Hydride generation/ICP-Optical Emission Spectrometry)

## 6.7.2.1 Principle

The sample salt is treated with hydrochloric acid and arsenic in the resultant solution is converted to arsenic hydride with a hydride generator and sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength of 193.696 nm is detected with the spectrometer and the emission intensity at this wavelength is measured to determine arsenic.

## 6.7.2.2 Apparatus

- (1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer)
- (2) A hydride generator

A continuous type hydride generator that is connectable to an ICP spectrometer (1) shall be used. An

example of a continuous type apparatus is shown in Fig. 6.



Fig. 6 An example of continuous type hydride generator

# 6.7.2.3 Reagents

(1) Hydrochloric acid (1+1)

Use the reagent for analysis of arsenic (JIS K 8180) with suitable dilution with water.

(2) Sodium tetrahydroborate solution  $(10g/L)^{(1)}$ 

Dissolve 5 g of sodium tetrahydroborate (NaBH<sub>4</sub>) in sodium hydroxide solution (0.1 mol/L) and dilute it with water to 500 mL. Prepare this solution every time when it is used.

(3) Standard solution of arsenic (0.2  $\mu$ g/mL)

Measure off exactly 10 mL of the standard solution of  $\operatorname{arsenic}(2 \ \mu g/mL)$  specified in item 6.7.1.3(2), transfer it to a 100- mL measuring flask, and dilute the solution to the mark with water.

(4) Argon gas

6.7.2.4 Procedure

(1) Weigh out approximately 10 g of the sample salt exactly, dissolve it in 40 mL of water and 10 mL of hydrochloric acid (1+1), and boil the solution for 10 minutes.

(2) Cool the solution, transfer it to a 100-mL measuring flask, and dilute the solution to the mark with water to obtain the sample solution.

(3) Connect a hydride generator to a ICP spectrometer, add sodium tetrahydroborate solution (10 g/L) and hydrochloric acid  $^{(1)}$  to the vessel, and activate the apparatus regulated in accordance with its manual.

(4) Generate arsenic hydride (arsine) by continuous introduction of the sample solution, spray it into the plasma torch, and measure the emission intensity at the wavelength of 193.696 nm to determine the amount of arsenic ( $\mu$ g) from the calibration curve prepared separately.

(5) Prepare the blank solution without the addition of the sample salt and measure the blank value for arsenic in the same manner as described above, and obtain the (net) amount of arsenic ( $\mu$ g) by subtracting the blank value from the determined amount of arsenic.

## 6.7.2.5 Preparation of Calibration Curve

(1) Measure off stepwise definite volumes of the standard solution of arsenic (0.2  $\mu$ g/mL) exactly within the range of 2 to 20 mL<sup>(2)</sup>, transfer each of them to a 100-mL measuring flask, and add 10 mL of hydrochloric acid (1+1) and 10 g of sodium chloride to each solution.

(2) After dissolving the sodium chloride completely, dilute each solution to the mark with water. Carry out the procedure specified in items 6.7.2.4(3) and (4) to determine the relationship between the amount of the arsenic (µg) and the emission intensity ratio to obtain the calibration curve.

## 6.7.2.6 Calculation and Expression

The content of the arsenic is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Arsenic (mg/kg) = 
$$\frac{\text{Amount of arsenic obtained (µg)}}{\text{Amount of sample salt used (g)}} \times f_A$$

# 6.7.2.7 Remarks

(1) Chose suitable concentrations of hydrochloric acid and sodium tetrahydroborate to the apparatus used for hydride generation, as the necessary concentrations of these vary depending on the apparatus used.

(2) Adjust the concentration and the volume of the standard solution used in the preparation of the calibration curve in accordance with the sensitivity of the apparatus for arsenic.

# 7. REFERENCE METHODS

# 7.1 Ignition Loss (Method of heating at 600 °C)

# 7.1.1 Principle

Ignition loss of the sample salt is the weight loss on heating at 600 °C corrected by the amount of magnesium chloride decomposed. This method shall be applied to the salt expected to contain much liquid inclusion in crystal or much crystal water <sup>(1)</sup>.

# 7.1.2 Apparatus

(1) An electric furnace

Use the one capable of being controlled at  $600\pm20$  °C.

(2) An electric drying oven: the one specified in item 4.2.2(1).

(3) Porcelain crucibles with outer lids: those of about 50 mm in diameter at the brim, about 31 mm in depth, and with porcelain inner lids of about 35 mm in diameter.

## 7.1.3 Procedure

(1) Heat a porcelain crucible with inner and outer lids at about 600 °C until a constant weight is reached  $^{(2),(3)}$ . Immediately after the sample salt is prepared, put approximately 5 g of the sample salt into the crucible, put on the inner and outer lids, and weigh the crucible with the sample salt inside accurately.

(2) After sliding the outer lid, dry the sample salt for approximately 90 minutes in an electric drying oven

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that has been preheated to about 140 °C.

(3) Place the inner lid on the sample salt <sup>(4)</sup>, put on the outer lid, and ignite the sample salt for 120 minutes in the electric furnace controlled at about 600 °C.

(4) Allow the crucible to cool to room temperature in a desiccator and weigh it accurately.

7.1.4 Calculation and Expression

(1) The equivalent amount of magnesium chloride (%) is obtained in advance as follows:

Calculate the equivalent amount of magnesium chloride (%) on the basis of the following equations from the analytical results (%) obtained in accordance with items 4.5 and 4.6 and round off it to 3 places of decimals. When the equivalent amount of magnesium chloride (%) calculated with the equation in (b) is zero or negative, omit it assuming that magnesium chloride is non-existent.

(a) In case of Ca(%) – SO<sub>4</sub>(%) × 0.417  $\geq 0$ 

Equivalent amount of magnesium chloride  $(\%) = Mg(\%) \times 3.92$ 

(b) In case of Ca(%) – SO<sub>4</sub>(%) × 0.417 < 0

Equivalent amount of magnesium chloride (%) =  $Ca(\%) \times 2.38 + Mg(\%) \times 3.92 - SO_4(\%) \times 0.99$ (2) Ignition loss (%) is calculated on the basis of the following equation <sup>(5)</sup>, compared with the tolerance, and reported in accordance with item 2.6.

> Ignition loss (%) =  $\frac{\text{Weight difference before and after ignition (g)}}{\text{Amount of sample salt used (g)}} \times 100$ - equivalent amount of magnesium chloride (%) × C

where C is the correction factor for magnesium chloride whose value is: C = 0.40 when the equivalent amount of magnesium chloride is 0 to 0.20 %, and C = 0.52 when it is 0.20 % or more.

(3) Tolerance

Ignition loss (%)	Tolerance (%)
less than 1.00	0.100
1.00 to 5.00	0.200
5.00 or more	0.350

# 7.1.5 Remarks

(1) The content of water in the sample salt is obtained in an approximate manner in this method. The method shall not be applied to sample salts containing organic matters (additives) because their weights are included in the ignition loss.

(2) A constant weight of a porcelain crucible shall be reached as follows:

Put the porcelain crucible with its lids into hydrochloric acid (1+4) in a beaker and heat the beaker to remove soluble matter adhering to the crucible. Wash the crucible with water, dry it, and carry out blank ignition of it at 600 °C or higher for about 3 hours. Allow the crucible to cool in a desiccator and weigh it.

Carry out blank ignition of the crucible at 600 °C for about 30 minutes again, allow it to cool in a desiccator, and weigh it to check whether its weight becomes constant (within $\pm 1$  mg) or not. If it does not, repeat these procedures.

(3) The crucible is to be placed near the center of the electric furnace and on a bisque sheet or a triangle stand so as not to touch the floor of the furnace directly.

(4) In case the sample salt with much liquid inclusion in crystal is to be treated, carry out item 7.1.3(3) with high caution. This is because powders of such salt are apt to burst while ignited and splatter, which is a cause of the error on the measured value.

(5) The values of the correction factor, C, for magnesium chloride (0.40 and 0.52) in the equation of item 7.1.4(2) have been determined from the degrees of decomposition of magnesium chloride hydrate into magnesium oxide obtained in the measurements of ignition losses of many salt samples by the present method.

7.2 Chloride Ion (Titration with Silver Nitrate Solution: Potentiometric Titration)

# 7.2.1 Principle

The sample salt is dissolved in water. The sample solution is made slightly acidic to neutral and then titrated with a silver nitrate standard solution using a potentiometric titrator. The potential difference is measured to determine the end point of this titration.

# 7.2.2

## Apparatus

(1) Potentiometric titrator

Use a system with the following components, (a) to (d)  $^{(1)}$ .

(a) Burette

A burette with a capacity of 20 mL or more is used.

(b) Electrodes

A sliver electrode is used for the indicator electrode, while a silver-silver chloride electrode is used for the reference electrode, and potassium nitrate is used for the salt bridge of the reference electrode <sup>(2)</sup>.

- (c) Potentiometer
- (d) Magnetic stirrer
- (2) Titration beaker

Use a 200-mL beaker.

## 7.2.3 Reagent

(1) Standard solution of sodium chloride  $(0.1 \text{ mol/L})^{(3)}$ 

Heat a platinum crucible to 600 °C until a constant weight is reached. Put approximately 5.9 g of the standard reagent of sodium chloride (NaCl) (JIS K 8005) in the crucible, heat the crucible to 600 °C for 1 hour, allow it to cool in a desiccator for 30 to 60 minutes, and then weigh it accurately. Dissolve all of the heated sodium chloride in water, transfer the solution to a 1-L measuring flask, and then dilute it to the mark with water. The factor  $f_{\text{NaCl}}$  of the solution is calculated down to 5 decimal places and rounded off to 4

decimal places on the basis of the following equation.

$$f_{\text{NaCl}} = \frac{\text{Amount of sodium chloride used (g)}}{5.8443} \times \frac{\text{Purity of sodium chloride used (\%)}}{100.00}$$

(2) Standard solution of silver nitrate  $(0.1 \text{ mol/L})^{(4)}$ 

Dissolve 17 g of silver nitrate (AgNO<sub>3</sub>) in 1 L of water and then store the solution in a brown-colored bottle. The chloride ion titer,  $F_{Cl}$  (mg), per 1 mL of this solution, shall be determined as follows:Measure off 25 mL of the standard solution of sodium chloride (0.1 mol/L), put the weighed solution into a beaker for titration, and then dilute it to approximately 80 mL with water. Soak the indicator electrode in the diluted solution, and then slowly titrate the solution with a standard solution of silver nitrate, while stirring it. The point at which the rate of change of the potential difference becomes a maximum is considered to be the endpoint. The consumption of the standard solution in this case is denoted by *a* mL.  $F_{Cl}$  (mg) is calculated down to 5 decimal places and then rounded off to 4 decimal places according to the following equation.

 $F_{\rm Cl}(\rm mg) = 3.5453 \times f_{\rm NaCl} \times 25.00/a$ 

#### 7.2.4 Procedure

(1) Measure off exactly 10 mL of the sample solution  $^{(5)}$  that was prepared according to the procedure described in item 4.1, transfer it to a flask for titration, and then dilute it to approximately 80 mL with water. (2) Soak the indicator electrode in the diluted solution, and then slowly titrate the solution with a standard solution of silver nitrate (0.1 mol/L), stirring it quickly but not to the extent that it splashes. The point at which the rate of change of the potential difference becomes a maximum is considered to be the endpoint. The consumption of the standard solution in this case is denoted by A mL.

## 7.2.5 Calculation and Expression<sup>(6)</sup>

(1) The content of the chloride ion (%) is calculated using the following equation  $^{(7)}$ , compared with the tolerance, and then reported as described in item 2.6

Chloride ion (%) = 
$$\frac{F_{Cl} \times A \times 5}{\text{Amount of sample salt used (g)}}$$

(2) Tolerance

Chloride ion (%)	Tolerance (%)
25.00 or more	0.15

#### 7.2.6 Remarks

(1) An automatic titrator can be used.

(2) It is recommended that the performance of the electrodes be checked in advance by the following method. Heat the standard reagent of sodium chloride (NaCl) (JIS K 8005) to 600 °C for 1 hour, and then allow it to cool in a desiccator. Then, carefully weigh out 0.2 g of the reagent and transfer it to a 200-mL beaker. Add 80 mL of water to dissolve the reagent, titrate the diluted solution with the standard solution of sliver nitrate

(0.1 mol/L) for which the factor is known, and then determine the content of the chloride ion (%). Repeat this process at least five times and then check that the average of the determined percentages is within the range of the certified values. A combined reference/indicator electrode can be used. An electrode with different specifications may also be used provided its performance can be confirmed.

(3) A standard solution of sodium chloride (0.1 mol/L) can also be prepared according to the following procedure.

Weigh out approximately 5.9 g of the standard reagent of sodium chloride (NaCl) (JIS K 8005), transfer it to a porcelain crucible, heat it to 600 °C for 1 hour, and then allow it to cool in a desiccator for 30 to 60 minutes. Transfer the total amount of heated sodium chloride into a weighing bottle and then weigh it precisely. Dissolve it in water, transfer the solution to a 1-L measuring flask, and then dilute it to the mark with water.

(4) Check the standardization of the standard solution of silver nitrate (0.1 mol/L) before each analysis.

(5) In the case where the sample solution is alkaline, add nitric acid (0.1 mol/L) to the solution to make it slightly acid to neutral before starting the titration.

(6) With the present method, the amounts of bromide and iodide ions are measured as equivalent amounts of chloride ions. In the case where the amounts of bromide and iodide ions are to be determined to correct the content of the chloride ion, calculate the equivalent volumes of the standard solution of silver nitrate (0.1 mol/L) and then deduct them from the titration volume A, according to the following equations. They are to be calculated down to 3 decimal places and rounded off to 2 decimal places.

Titration volume equivalent to the amount =  $\frac{\text{Bromide ion obtained (\%)} \times \text{Amount of sample salt used (g)}}{5 \times F_{\text{Cl}} \times 2.2538}$ 

Titration volume equivalent to the amount =  $\frac{\text{Iodide ion obtained (\%)} \times \text{Amount of sample salt used (g)}}{5 \times F_{\text{Cl}} \times 3.5795}$ 

In the case where the sample contains phosphate or sulfide ions, a silver compound will be formed, which may cause an error. When the sample containing large amounts of iodide or sulfide ions, silver iodide or silver sulfide firmly adheres to the silver electrode. In this case, it is possible for the potential of the electrode to be read incorrectly.

(7) The equation in item 7.2.5(1) summarizes the following equation.

Chloride ion (%) = 
$$\frac{\frac{F_{c1} \times A \times 100}{1000}}{\frac{Amount of sample salt used (g) \times 10 (Volume of sample solution used, mL)}{500 (Volume of solution w hen sample salt is dissolved, mL)}$$

# 7.3 Sulfate Ion (Gravimetry)

7.3.1 Principle

The sample salt is dissolved in water and barium chloride solution is added to the solution to form the precipitate of barium sulfate. The precipitate is ignited and weighed to determine the sulfate ion. This method is applicable when the content of the sulfate ion is 0.04 to 3.0 %.

# 7.3.2 Apparatus

(1) An electric furnace

Use the one capable of being controlled between 600 and 700 °C and with good ventilation.

(2) Crucibles: platinum or porcelain crucibles for chemical analysis.

# 7.3.3 Reagents

- (1) Hydrochloric acid (1+1)
- (2) Barium chloride solution (8.5 %)

Dissolve 10 g of barium chloride dihydrate (BaCl<sub>2</sub> $\cdot$ 2H<sub>2</sub>O) in water and dilute the solution to 100 mL with water.

## 7.3.4 Procedure

(1) Weigh out approximately 10 g of the sample salt exactly, transfer it to a 300-mL beaker, and dissolve it with approximately 200 mL of warm water as much as possible while stirring thoroughly.

(2) Filter the solution through a filter paper, receive the filtrate with a 500-mL beaker, and wash the 300-mL beaker and the filter paper with water a few times.

(3) Add 2 mL of hydrochloric acid (1+1) to the filtrate, boil it, and, while stirring, add drop by drop 20 mL of barium chloride solution (8.5 %) which has been heated separately. After boiling the solution for a while, allow it to stand on a hot water bath for about 1 hour <sup>(1)</sup>.

(4) Filter the precipitate through a filter paper (No. 5C) and wash it with hot water thoroughly. Take out a few mL of the last portion of the washing water used, and after adding to it a few drops of nitric acid, add silver nitrate solution drop by drop to confirm that the reaction of the chloride ion is hardly recognized. In case the chloride ion is detected, wash the precipitate a few more times. However, the total volume of the filtrate and washing water shall not exceed 250 mL.

(5) Put the precipitate, together with the filter paper, in the crucible  $^{(2)}$  of which a constant weight has been reached. In the beginning, incinerate the precipitate and the filter paper at a low temperature and then, ignite them for 40 minutes in the electric furnace controlled at 700 to 800 °C  $^{(3)}$ .

(6) Cool the crucible to room temperature in a desiccator and weigh it accurately.

## 7.3.5 Calculation and Expression

(1) The content of the sulfate ion (%) is calculated on the basis of the following equation <sup>(4)</sup>, compared with tolerance and reported in accordance with item 2.6.

# Sulfate ion (%) = $\frac{\text{Amount of precipitat e obtained } (g) \times 41.16}{\text{Amount of sample salt used } (g)}$

# (2) Tolerance

Sulfate ion (%)	Tolerance
less than 0.20	0.030
0.20 to 3.00	0.040

# 7.3.6 Remarks

(1) Instead of being allowed to stand on the hot water bath for 1 hour, the solution may be allowed to stand at room temperature for 12 hours.

(2) A constant weight of a platinum crucible can be reached in a short time. A constant weight of a porcelain crucible shall be reached in the procedure specified in items 7.1.5(2) and (3).

(3) A gas burner may be used for igniting the precipitate. In this case, it shall be regulated such that the bottom of the crucible turns red.

(4) The equation in item 7.3.5(1) is obtained by rearranging the following equation:

Sulfate ion (%) = 
$$\frac{\text{Amount of precipitate obtained (g)} \times 0.4116}{\text{Amount of sample salt used (g)}} \times 100$$

# 7.4 Potassium and Sulfate Ion (ICP-Optical Emission Spectrometry)

# 7.4.1 Principle

The sample salt is dissolved in water, and the resultant solution is sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength characteristic of potassium or sulfur is detected and the emission intensity at the characteristic wavelength is measured to determine potassium or sulfate ion.

# 7.4.2 Apparatus

(1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer)

The apparatus shall be used with a plasma torch and a nebulizer for high salt concentration, regulated in accordance with its manual.

## 7.4.3 Reagents

- (1) Standard solutions of potassium and sulfate ion: the ones specified in Chapter 4.
- (2) Sodium chloride: the standard reagent of sodium chloride (NaCl) (JIS K 8005)

(3) Argon gas

7.4.4 Procedure<sup>(1)</sup>

(1) Prepare the sample solution in accordance with item  $4.1^{(2),(3)}$ .

(2) Regulate the ICP spectrometer, spray the sample solution in the plasma torch, and measure the emission intensity <sup>(6)</sup> at the wavelength characteristic of potassium or sulfur <sup>(4), (5)</sup>. Obtain the amount of potassium or the sulfate ion (mg) from the calibration curve prepared separately.

7.4.5 Preparation of Calibration Curve

(1) Measure off stepwise definite volumes of the standard solution of the component to be determined within the application range specified in Table 8 exactly <sup>(7)</sup>, transfer the solutions to respective 100-mL measuring flasks, and add 2 g of sodium chloride to each solution.

(2) After dissolving the sodium chloride completely, dilute to the mark with water. Carry out the procedure specified in item 7.4.4(2) to determine the relationship between the amount of the component (mg) and the emission intensity to obtain the calibration curve.

Table 8 Calibration ranges and application ranges

Component	Calibration range (mg/100 mL)	Application range (%)
Potassium	1.0 to 5.0	0.05 to 0.25
Sulfate ion	0.2 to 5.0	0.01 to 0.25

7.4.6 Calculation and Expression

(1) The content of the component (%) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Component (%) = 
$$\frac{\text{Amount of component obtained (mg)}}{\text{Amount of sample salt used (g)}} \times 0.5 \times f$$

where f is the factor of the standard stock solution of each component.

(2) Tolerance

Component (%)	Tolerance (%)
less than 0.10	0.010 %
0.10 or more	0.020 %

# 7.4.7 Remarks

(1) In case the content of potassium is lower than the lower limit of the application range in Table 8 potassium shall be determined by the method specified in item 4.7 or 5.3.2, due to the low sensitivity of the ICP method for potassium. The sensitivity for potassium may be improved by optimizing measuring conditions. Note in that case, however, that sensitivity for other elements to be determined simultaneously is also altered.
 (2) In case the sample solution contains insoluble matter, filter it with a dried filter paper (No. 5C). In this
case, discard the first 5 mL of the filtrate and use the rest for the analysis.

(3) In case the nebulizer is plugged while spraying the sample solution, decrease the amount of the sample salt or filter the sample solution before use.

(4) Sulfate ion is determined by measuring the emission intensity of sulfur (S) at the wavelength of 180.73 nm in the ultraviolet region. In this case, the inside of the spectrometer shall be filled with inert gas or evacuated to enhance the sensitivity, thus making this method applicable to the analysis of sample salts with low contents of sulfate ion.

(5) Refer to Appendix I to select the wavelength to be used. When the high order spectral lines can be used in the apparatus, they may be used for the analysis. In the selection of the wavelength for an element, make sure that there is no interference from closely located spectral lines of other elements.

(6) The background correction must always be done to obtain accurate emission intensity.

(7) Adjust the concentrations of the standard solutions for the calibration curve in accordance with the sensitivity of the apparatus for the element to be determined and its content in the sample solution.

7.5 Particular Trace Components (ICP-Optical Emission Spectrometry)

#### 7.5.1 Principle

The sample salt is treated with nitric acid and the resultant solution is sprayed into the inductively coupled plasma of argon formed by a high frequency. The emission at the wavelength characteristic of the element to be determined is detected and the emission intensity at the characteristic wavelength is measured to determine the element. This method is applied to the determination of aluminum, barium, chromium, iron, manganese, nickel, silicon, strontium, vanadium and zinc.

#### 7.5.2 Apparatus

(1) An inductively coupled plasma optical emission spectrometer (ICP spectrometer)<sup>(1)</sup>

The apparatus shall be used with a plasma torch and a nebulizer for high salt concentration. It should be capable of monitoring at two wavelengths in parallel and is regulated in accordance with the manual. 7.4.3 Reagents

(1) Yttrium solution (10  $\mu$ g/mL)

Weigh out approximately 0.318 g of yttrium oxide  $(Y_2O_3)$ , dissolve it with 5 mL of ultra pure nitric acid (JIS K 9901) with heating, cool the solution, transfer it to a 250-mL measuring flask, and dilute it to the mark with water. Measure off exactly 5 mL of the solution, transfer it to a 500-mL measuring flask, and dilute it to the mark with water.

(2) Standard solutions of elements to be determined

Standard solutions of the elements to be determined shall be prepared in accordance with Appendix II.

- (3) Standard reagent of sodium chloride (NaCl) (JIS K 8005)
- (4) Argon gas
- (5) Nitric acid (1+1)
- 7.5.4 Procedure<sup>(2)</sup>

(1) Weigh out approximately 10 g of the sample salt exactly, dissolve it with 40 mL of water and 10 mL of nitric acid (1+1), and boil the solution for 10 minutes.

(2) Cool the solution, transfer it to a 100-mL measuring flask, add 10 mL of yttrium solution (10  $\mu$ g/mL), and dilute the solution to the mark with water to obtain the sample solution <sup>(3)</sup>.

(3) Regulate the apparatus, spray the sample solution in the plasma torch <sup>(4)</sup>. measure the emission intensity at the wavelength characteristic of the element to be determined and that at the wavelength of 371.029 nm for yttrium in parallel <sup>(5),(6)</sup>.

(4) Divide the emission intensity of the element by that of yttrium to obtain the emission intensity ratio, and obtain the amount of the element ( $\mu$ g) from a calibration curve prepared separately.

#### 7.5.5 Preparation of Calibration Curve

(72)

(1) Measure off stepwise definite volumes of the standard solution of the element to be determined exactly <sup>(7)</sup>, transfer each of them to a 100-mL measuring flask, and add 10 mL of nitric acid (1+1), 10 mL of yttrium solution (10  $\mu$ g/mL) and 10 g of sodium chloride to each solution.

(2) After dissolving the sodium chloride completely, dilute each solution to the mark with water. Carry out the procedure specified in items 7.5.4(3) and (4) to determine the relationship between the amount of the element ( $\mu$ g) and the emission intensity ratio to obtain the calibration curve.

#### 7.5.6 Calculation and Expression

The content of the element (mg/kg) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Element (mg/kg) = 
$$\frac{\text{Amount of element obtained } (\mu g)}{\text{Amount of sample salt used } (g)} \times f$$

where f is the factor of the standard stock solution of the element to be determined.

#### 7.5.7 Remarks

(1) In case the apparatus is incapable of measuring two or more emission intensities in parallel, measure the emission intensities of the element to be determined and yttrium sequentially and obtain the emission intensity ratio.

(2) In case silicon is determined, the sample solution shall be prepared as follows: Weigh out approximately 1 g of the sample salt exactly, transfer it to a 100-mL measuring flask, and add 10 mL of water to dissolve it. Add 2.5 mL of hydrochloric acid (1+10) and 2 mL of hydrofluoric acid (1+9), and allow the solution to stand for 10 minutes. Add 50 mL of boric acid solution (4 %), add 10 mL of yttrium solution (10  $\mu$ g/mL), and dilute the solution to the mark with water. A nebulizer for hydrofluoric acid shall be used instead of the one for high salt concentration.

(3) In case the sample solution contains insoluble matter, filter it with a dried filter paper (No. 5C). In this case, discard the first 5 mL of the filtrate and use the rest for the analysis.

(4) In case the nebulizer is plugged while spraying the sample solution, decrease the amount of the sample salt used or filter the sample solution before use.

(5) The background correction must always be done to obtain accurate emission intensity.

(6) Refer to Appendix I to select the wavelength to be used. When the high order spectral lines can be used in the apparatus, they may be used for the analysis. In the selection of the wavelength for an element, make sure that there is no interference from closely located spectral lines of other elements.

(7) Adjust the concentration and the volume of the standard solution of the element to be determined used in the preparation of the calibration curve in accordance with the sensitivity of the apparatus for the element.

#### 7.6 Bromide Ion (Iodometry)

#### 7.6.1 Principle

The sample salt is dissolved in water and the pH of the resultant solution is adjusted with sodium dihydrogenphosphate solution. The bromide ion in the solution is oxidized with sodium hypochlorite solution and determined by titrating iodine liberated with sodium thiosulfate solution after adding potassium iodide. This method is applicable when the content of the bromide ion is 10 to 2,000 mg/kg.

#### 7.6.2 Apparatus

(1) Burettes

(2) Erlenmeyer flasks with ground-in stoppers: ones with 200-mL capacity (JIS R 3503).

#### 7.6.3 Reagents

(1) Standard stock solution of bromide ion (0.5 mg/mL)

Dry about 2 g of sodium bromide (NaBr) at 110 °C for about 2 hours, and allow it to cool in a desiccator. Weigh out approximately 0.64 g of dried sodium bromide exactly, and dissolve it in water. Transfer the solution to a 1-L measuring flask and dilute it to the mark with water. The factor of this solution,  $f_{Br}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

 $f_{\rm Br}$  = Amount of sodium bromide used (g)/0.644

(2) Standard stock solution of bromate ion (0.5 mg-Br/mL)

Dry about 2 g of potassium bromate (KBrO<sub>3</sub>) at 110 °C for about 2 hours, and allow it to cool in a desiccator. Weigh out approximately 1.0 g of dried potassium bromate exactly, and dissolve it in water. Transfer the solution to a 1-L measuring flask and dilute it to the mark with water. The factor of this solution,  $f_{BrO3}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

 $f_{BrO3}$  = Amount of potassium bromate used (g)/1.045

(3) Sodium hypochlorite solution  $(0.5 \text{ mol/L})^{(1)}$ 

Measure off exactly 25 mL of the standard stock solution of bromate ion (0.5 mg-Br/mL), transfer it to

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a 200-mL Erlenmeyer flask with a ground-in stopper, add 2 g of sodium dihydrogenphposphate dihydrate, and carry out items 7.6.4(3) and (4) on the solution. The consumption of the standard solution of sodium thiosulfate is denoted as "*a*" mL. The bromate ion titer,  $F_{\text{BrO3}}$  (Br-mg), per 1 mL of the standard solution of sodium thiosulfate is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$F_{\text{BiO3}}$$
 (Br - mg) =  $25 \times f_{\text{BiO3}} \times 0.5/a$  (mL)

Measure off exactly 1 mL of sodium hypochlorite (NaClO) solution, transfer it to a 250-mL measuring flask, and dilute it to the mark with water. Measure off exactly 10 mL of this solution, add 50 mL of water, 2 g of potassium iodide and 10 mL of acetic acid (1+2) to it, allow the solution to stand for about 1 minute, and carry out item 7.6.4(4) on it. The consumption of the standard solution of sodium thiosulfate is denoted as "*b*" mL.

Sodium hypochlorite (NaClO) solution (0.5 mol/L) is prepared as follows:

(a) First, calculate the amount of sodium hypochlorite, D (g), contained in 1 mL of sodium hypochlorite solution on the basis of the following equation:

$$D(g) = \frac{F_{\text{BrO3}} (\text{Br} - \text{mg}) \times 2.80 \times b (\text{mL})}{1 \times \frac{10}{250} \times 1000} = F_{\text{BrO3}} (\text{Br} - \text{mg}) \times 0.070 \times b (\text{mL})$$

where  $2.80 = 3 \times \text{NaClO} / \text{Br}$ 

(b) Then, measure off exactly K mL of sodium hypochlorite solution (standard stock solution of sodium hypochlorite) calculated on the basis of the following equation, transfer it to a 100-mL measuring flask and dilute it to the mark with water to obtain sodium hypochlorite solution (0.5 mol/L).

$$K(ml) = 3.72/D$$

where 3.72 is the amount of sodium hypochlorite (g) contained in 100 mL of sodium hypochlorite solution (0.5 mol/L).

(4) Standard solution of sodium thiosulfate

Weigh out 10 g of sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O), dissolve it with water which has been boiled to remove carbon dioxide in advance, dilute the solution to 1 L, and allow the solution to stand for about 1 hour. The bromide ion titer,  $F_{Br}$  (mg), per 1 mL of this solution is determined as follows:

Measure off exactly 5 mL of the standard stock solution of bromide ion (0.5 mg/mL), transfer it to a 200-mL Erlenmeyer flask with a ground-in stopper, add 50 mL of water and 2 g of sodium dihydrogenphosphate, and carry out items 7.6.4(2) to (5) on the solution. The consumption of the standard solution of sodium thiosulfate is denoted as "*c*" mL.  $F_{\rm Br}$  (mg) is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$F_{\rm Br} \,({\rm mg}) = 5 \times f_{\rm Br} \times 0.5 / (c - B)$$

where B is the titration volume (the consumption of the standard solution of sodium thiosulfate) in the blank test in item 7.6.4(5).

(5) Starch solution

Mix 1 g of soluble starch with 5 mL of water, add the mixture to about 200 mL of hot water while stirring, boil the solution for 1 minute, and allow it to cool. Prepare this solution every time when it is used. (6) Hexaammonium heptamolybdate solution

Dissolve 2 g of hexaammonium heptamolybdate tetrahydrate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] with a mixture of 60 mL of water and 5 mL of ammonia water (1+3), add and dissolve 24 g of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>),

and dilute the solution to 100 mL with water.

- (7) Sodium dihydrogenphosphate dihydrate (NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O)
- (8) Potassium iodide (KI)
- (9) Sodium formate solution (50 %)

Dissolve 50 g of sodium formate (HCOONa) with water and dilute the solution to 100 mL with water. (10) Sulfuric acid (1+5)

(11) Acetic acid (1+2)

#### 7.6.4 Procedure

(1) Take out about 5 g of the sample salt, weigh it exactly, transfer it to a 200-mL Erlenmeyer flask with a ground-in stopper, dissolve it with approximately 50 mL of water, and add and dissolve 2 g of sodium dihydrogenphosphate dihydrate.

(2) Add 5 mL of sodium hypochlorite solution (0.5 mol/L) and boil the solution for about 5 minutes. Add 5 mL of sodium formate solution (50 %), boil the solution for 5 minutes, and cool it to about room temperature.
(3) Add approximately 10 mL of water, 1 g of potassium iodide, 20 mL of sulfuric acid (1+5) and a few drops of hexaammonium heptamolybdate solution, and allow the solution to stand for about 1 minute in the flask with the stopper fixed.

(4) Titrate iodine liberated with the standard solution of sodium thiosulfate and, after the solution becomes pale yellow, add 1 mL of starch solution. The end point of the titration is when the color of the solution changes from purple to colorless <sup>(2)</sup>. The consumption of the standard solution of sodium thiosulfate is denoted by "A" mL.

(5) Carry out items 7.6.4(1) to (4) without sample salt. The consumption of the standard solution of sodium this sale is denoted by "B" mL.

#### 7.6.5 Calculation and Expression

The content of the bromide ion (mg/kg) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Bromide ion (mg/kg) = 
$$\frac{F_{Br} (mg) \times (A - B) \times 1000}{Amount of sample salt used (g)}$$

#### 7.6.6 Remarks

(1) The molarity of sodium hypochlorite solution (0.5 mol/L) need not be exactly 0.5 mol/L.

(2) Sometimes, the solution becomes blue again sometime after the end point is reached. This is considered due to the fact that iodine  $(I_2)$  is formed from hydrogen iodide (HI) in the solution through oxidation by the

air.

7.7 Hexacyanoferrate (II) (Ferrocyanide) (Prussian blue absorptiometry)

#### 7.7.1 Principle

The sample salt is dissolved in water, and the absorbance of Iron (III) hexacyanoferrate (II) formed by addition of iron (II) sulfate solution is measured to determined the hexacyanoferrate (II) ion <sup>(1)</sup>. This method is applicable when the content of the hexacyanoferrate (II) ion is 1.0 to 10 mg/kg.

7.7.2 Apparatus

(1) A photoelectric spectrophotometer or a photoelectric photometer

(2) Absorption cells: glass or quartz cells with optical path length of 50 mm.

7.7.3 Reagents

(1) Standard stock solution of hexacyanoferrate (II) ion (1 mg/mL)

Weigh out approximately 1.0 g of potassium hexacyanoferrate (II) trihydrate  $[K_4Fe(CN)_6 \cdot 3H_2O]$  exactly, dissolve it in water, transfer the solution to a 500-mL measuring flask, and dilute it to the mark with water. The solution is to be stored in a brown-colored bottle in a cool and dark place. The factor of this solution,  $f_{Fe(CN)6}$ , is calculated down to 3 places of decimals and rounded off to 2 places of decimals on the basis of the following equation:

 $f_{\text{Fe(CN)6}} = \frac{\text{Amount of potassium hexacyanoferrate(II)trihydrate used (g)}}{1.993}$ 

(2) Standard solution of hexacyanoferrate (II) ion (50  $\mu$ g/mL)

Measure off 5 mL of the standard stock solution of hexacyanoferrate (II) ion (1 mg/mL) exactly, transfer it to a 100-mL measuring flask and dilute it to the mark with water.

(3) Iron (II) sulfate solution

Dissolve 3 g of iron (II) sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ) in 80 mL of water, add 1 mL of sulfuric acid, and dilute the solution to 100 mL with water. Filter the solution with a No. 5C filter paper before use. Prepare this solution every time when it is used.

(4) Sodium chloride (NaCl)

#### 7.7.4 Procedure

(1) Weigh out approximately 20 g of the sample salt exactly, transfer it to a 100-mL beaker, and dissolve it with 80 mL of water.

(2) Filter the solution with a No. 5C filter paper <sup>(2)</sup>, receive the filtrate in a 100-mL measuring flask. Rinse the filter paper with a small quantity of water (10 mL or less) and receive the used washing water in the same flask.

(3) Add 5 mL of iron (II) sulfate solution, dilute the solution to the mark with water, shake the solution thoroughly, and allow it to stand for 30 minutes. Transfer a portion of the solution to an absorption cell of 50 mm long, measure the absorbance at the wavelength of 720 nm with water as reference, and obtain the

amount of the hexacyanoferrate (II) ion ( $\mu$ g) from the calibration curve prepared separately.

#### 7.7.5 Preparation of Calibration Curve

Weigh out 10 g of sodium chloride, transfer it to a 50-mL measuring flask, and dissolve it with 40 mL of water. Repeat this five times to have five measuring flasks containing sodium chloride solution. Measure off exactly 0, 200, 600, 1,000 and 2,000  $\mu$ L of the standard solution of hexacyanoferrate (II) ion (50  $\mu$ g/mL) (correspondingly containing 0, 10, 30, 50 and 100  $\mu$ g of the hexacyanoferrate (II) ion), and add each of them to one of the measuring flasks on the one-to-one basis. Add 2.5 mL of iron (II) sulfate solution to each solution, dilute it to the mark with water, mix the solution thoroughly, and allow it to stand for 30 minutes. Measure the absorbance of each solution in the same manner as specified in item 7.7.4(3) and determine the relationship between the absorbance and the amount of the hexacyanoferrate (II) ion ( $\mu$ g) to obtain the calibration curve. Prepare the calibration curve every time when the sample solution is analyzed.

#### 7.7.6 Calculation<sup>(3)</sup> and Expression

The content of the hexacyanoferrate (II) ion (mg/kg) is calculated on the basis of the following equation, compared with the tolerance, and reported in accordance with item 2.6.

Hexacyanoferrate(II)ion (mg/kg) = 
$$\frac{\text{Amount of hexacyanoferrate(II)ion obtained }(\mu g) \times 2}{\text{Amount of sample salt used }(g)} \times f_{Fe(CN)}$$

#### 7.7.7 Remarks

(1) In case hexacyanoferrate (II) is to be detected qualitatively, carry out the following:

Carry out item 7.7.4 from the beginning up to the operation of allowing the solution to stand for 30 minutes specified in item 7.7.4(3). Filter the solution with suction using a membrane filter of pore size of 0.45  $\mu$ m and observe the color of the filter carefully. Hexacyanoferrate (II) in the sample salt is judged positive when the filter is colored in blue.

(2) In case insoluble matter is not recognized, filtration may be omitted.

(3) In case the content of the hexacyanoferrate (II) ion (mg/kg) is reported as the content of potassium hexacyanoferrate (II) (mg/kg) or sodium hexacyanoferrate (II) (mg/kg), calculate it on the basis of the following equations:

Potassium hexacyanoferrate (II)  $[K_4Fe(CN)_6]$  (mg/kg) = Hexacyanoferrate (II) ion (mg/kg) × 1.74 Sodium hexacyanoferrate (II)  $[Na_4Fe(CN)_6]$  (mg/kg) = Hexacyanoferrate (II) ion (mg/kg) × 1.43

### Appendix I Wavelengths commonly used in ICP-Optical Emission Spectrometry measurements

In the table below, wavelengths of ICP emission lines with high sensitivity are listed. The wavelength in boldface type is the one most commonly used for each of the elements due to minimal interference from coexisting elements. Another wavelength may be used if the precision and accuracy of the measured value at that wavelength has been confirmed in advance. Refer to JIS K 0116 for further details.

Element	Wavelength (nm)	Element	Wavelength (nm)	Element	Wavelength (nm)
Al	396.152	Cu	324.754	Pb	220.351
	309.271		327.396		216.999
	167.079		224.700		261.418
As	193.696	Fe	238.204	S	180.73
	197.197		239.562		
	228.812		259.904		
Ba	455.403	Hg	194.227	Si	251.611
	493.409		253.652		288.158
	233.527				212.412
Ca	393.367	Κ	404.721	Sr	407.771
	396.847		769.896		421.552
	422.673				216.596
Cd	214.438	Mg	279.553	V	309.311
	228.802		280.270		310.230
	226.502		285.213		292.402
Cr	205.552	Mn	257.610	Y	324.288
	206.149		259.373		321.669
	267.716		260.569		371.029
		Ni	221.647	Zn	213.856
			231.604		202.548
			232.003		206.200

#### Appendix II

# Preparation of standard stock solutions and standard solutions of particular trace components in item 7.5

Preparations of standard stock solutions and standard solutions of the elements categorized as particular trace components in Chapter 7 are summarized here.

1.1 Standard stock solution of aluminum (100 µg/mL)

Weigh out approximately 0.18 g of aluminum potassium sulfate dodecahydrate [AlK(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O] (potassium alum) exactly, dissolve it in sulfuric acid (0.003 mol/L), transfer the solution to a 100-mL measuring flask, and dilute it to the mark with sulfuric acid (0.003 mol/L). The factor of this solution,  $f_{Al}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

 $f_{AI} = \frac{\text{Amount of aluminum potassium sulfate dodecahydrate used (g)}}{0.176}$ 

1.2 Standard solution of aluminum (0.5 µg/mL)

Measure off exactly 0.50 mL of the standard stock solution of aluminum (100  $\mu$ g/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with sulfuric acid (0.003 mol/L).

1.3 Standard solution of aluminum (0.25 µg/mL)

Measure off exactly 0.25 mL of the standard stock solution of aluminum (100  $\mu$ g/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with sulfuric acid (0.003 mol/L).

1.4 Standard solution of aluminum (0.1  $\mu$ g/mL)

Measure off exactly 0.10 mL of the standard stock solution of aluminum (100  $\mu$ g/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with sulfuric acid (0.003 mol/L).

2.1 Standard stock solution of barium (0.1 mg/mL)

Weigh out approximately 0.18 g of barium chloride dihydrate (BaCl<sub>2</sub>·12H<sub>2</sub>O) exactly, dissolve it with water, transfer the solution to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Ba}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Ba} = \frac{\text{Amount of barium chloride dihydrate used (g)}}{0.178}$$

3.1 Standard stock solution of chromium (0.1 mg/mL)

Dry potassium dichromate ( $K_2Cr_2O_7$ ) at 100 to 110 °C for 3 to 4 hours and allow it to cool in a desiccator. Weigh out approximately 0.28 g of dried potassium dichromate exactly, dissolve it with water, transfer the solution to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Cr}$ , is calculated down to 3 places of decimals and rounded off to 2 places of decimals on the basis of the following equation:

$$f_{\rm cr} = \frac{\rm Amount \ of \ potassium \ dichromate \ used \ (g)}{0.283}$$

3.2 Standard solution of chromium  $(1 \mu g/mL)$ 

Measure off exactly 1 mL of the standard stock solution of chromium (0.1 mg/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with water.

4.1 Standard stock solution of iron (0.1 mg/mL)

Weigh out approximately 0.10 g of iron (Fe) (purity: 99.9 % or better) exactly, dissolve it in 30 mL of hydrochloric acid (1+1) with heating, cool the solution, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Fe}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Fe} = \frac{\text{Amount of iron used (g)}}{0.100} \times \frac{\text{Purity of iron used (\%)}}{100}$$

5.1 Standard stock solution of manganese (0.1 mg/mL)

Weigh out approximately 0.10 g of manganese (Mn) (purity: 99.9% or better) exactly, dissolve in a mixture of 10 mL of water and 25 mL of nitric acid (1+2) with heating. Boil the solution to expel nitrogen oxides, cool it, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Mn}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Mn} = \frac{\text{Amount of manganese used (g)}}{0.100} \times \frac{\text{Purity of manganese used (\%)}}{100}$$

#### 5.2 Standard solution of manganese (10 $\mu$ g/mL)

Measure off exactly 10 mL of the standard stock solution of manganese (0.1 mg/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with water.

6.1 Standard stock solution of nickel (0.1 mg/mL)

Weigh out approximately 0.10 g of nickel (Ni) (purity: 99.9% or better) exactly, dissolve in 25 mL of nitric acid (1+1) with heating. Boil the solution to expel nitrogen oxides, cool it, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Ni}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Ni} = \frac{\text{Amount of nickel used (g)}}{0.100} \times \frac{\text{Purity of nickel used (\%)}}{100}$$

6.2 Standard solution of nickel (10 µg/mL)

Measure off exactly 10 mL of the standard stock solution of nickel (0.1 mg/mL), transfer it to a 100-mL measuring flask, add 2 mL of nitric acid (1+1), and dilute the solution to the mark with water.

7.1 Standard stock solution of silicon dioxide (1 mg/mL)

Ignite silicon dioxide  $(SiO_2)$  at 900 to 1000 °C for about 1 hour and allow it to cool in a desiccator. Weigh out approximately 0.50 g of ignited silicon dioxide exactly, put it in a platinum crucible, add 4 g of sodium carbonate anhydride and mix powders thoroughly, and heat to fuse the mixture for about 30 minutes. After allowing the melt to cool, dissolve in water, transfer the solution to a 500-mL measuring flask, and dilute it to the mark with water. This standard stock solution of silicon dioxide (1 mg/mL) shall be stored in a polyethylene bottle. The factor of this solution,  $f_{SiO2}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm SiO2} = \frac{\text{Amount of silicon dioxide used (g)}}{0.500} \times \frac{\text{Purity of silicon dioxide (\%)}}{100}$$

7.2 Standard solution of silicon dioxide (0.1 mg/mL)

Measure off exactly 20 mL of the standard stock solution of silicon dioxide (1 mg/mL), transfer it to a 200-mL measuring flask, and dilute it to the mark with water. This solution shall be stored in a polyethylene bottle.

8.1 Standard stock solution of strontium (1 mg/mL)

Weigh out approximately 2.4 g of strontium nitrate  $[Sr(NO_3)_2]$  exactly, dissolve it with water, transfer the solution to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Sr}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm sr} = \frac{\text{Amount of strontium nitrate used (g)}}{2.415}$$

8.2 Standard solution of strontium (20 µg/mL)

Measure off exactly 5 mL of the standard stock solution of strontium (1 mg/mL), transfer it to a 250-mL measuring flask, and dilute it to the mark with water.

9.1 Standard stock solution of vanadium (0.1 mg/mL)

Weigh out approximately 0.23 g of ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>) exactly, dissolve in a mixture of 10 mL of sulfuric acid (1+1) and 200 mL of hot water, allow the solution to cool, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_V$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_v = \frac{\text{Amount of ammonium vanadate used (g)}}{0.230}$$

9.2 Standard solution of vanadium (2 µg/mL)

Measure off exactly 2 mL of the standard stock solution of vanadium (0.1 mg/mL), transfer it to a 100-mL measuring flask, and dilute it to the mark with water.

10.1 Standard stock solution of zinc (0.1 mg/mL)

Weigh out approximately 0.10 g of zinc (Zn) (JIS K 8005 or JIS H 2107) exactly, dissolve it with 25 mL of nitric acid (1+1) with heating. Boil the solution to expel nitrogen oxides, cool it, transfer it to a 1-L measuring flask, and dilute it to the mark with water. The factor of this solution,  $f_{Zn}$ , is calculated down to 4 places of decimals and rounded off to 3 places of decimals on the basis of the following equation:

$$f_{\rm Zn} = \frac{\text{Amount of zinc used (g)}}{0.100} \times \frac{\text{Purity of zinc used (\%)}}{100}$$

10.2 Standard solution of zinc (1  $\mu$ g/mL)

Measure off exactly 5 mL of the standard stock solution of zinc (0.1 mg/mL), transfer it to a 500-mL measuring flask, add 10 mL of nitric acid (1+1), and dilute the solution to the mark with water.

## METHODS FOR SALT ANALYSIS 5th edition

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